Synthesis and Characterization of Thermally Stable Nanoporous Gallium Oxide Phases

Chinmay A. Deshmane and Moises A. Carreon*

Department of Chemical Engineering, University of Louisville, Louisville KY 40292

*Corresponding author: macarr15@louisville.edu

Introduction:

Mesostructured metal oxides are not only useful as catalysts and separating or adsorbing agents, but also as functional host materials with unique optical, electrical, or magnetic properties, owing to the shape-specific and/or quantum effects of their thin inorganic skeletons [1]. In particular, gallium oxide is a wide-band-gap semiconductor (Eg = 4.9 eV) that exhibits luminescence and conduction properties with potential applications in optoelectronic devices, high-temperature stable gas sensors and high- temperature/high-power electronic devices [2]. Gallium oxide is a strong acid catalyst [1]. It has been used as a catalyst for the oxidative dehydrogenation of ethane to ethane and propane to propene [3]. Ga_2O_3-based catalysts are active in in the selective catalytic reduction of NO_x by hydrocarbons in the presence of oxygen [4]. Supported gallium oxides are preferred over zeolites in the de-NO_x reaction because of their weaker acidity [5]. These catalysts are also effective in the aromatization of ethane in the presence of CO_2 [3].

Recently, gallium oxide has been synthesized by both chemical and physical methods. However, these methods exhibited limited control over crystal size, homogeneity, and surface area. Mesoporous gallium oxide has been synthesized using diverse techniques, such as thermal decomposition [6], homogeneous precipitation using ammonia [1, 7, 8], and surface layer adsorption [2]. Yada et al. [7] synthesized mesostructured gallium oxide, with hexagonal and layered structures by the homogeneous precipitation method using urea and sodium dodecyl sulfate as the structure directing agent (SDA). Although the material that was obtained was ordered at the mesoscale, it showed poor crystallinity and was thermally unstable at temperatures above 400^{o}C. Areán et al. [8] prepared mesoporous gallium oxide with cubic spinel type structure via homogeneous precipitation using ammonia. The material showed relatively high surface area (120 m^2/g) and a pore diameter of 4.2 nm. However, these phases displayed inhomogeneous crystal size and lacked unimodal pore size distribution.

In the present work, we report the synthesis and characterization of mesoporous gallium oxide via evaporation-induced self-assembly (EISA) [9]. This technique eliminates the need for high synthesis temperatures commonly required for solid-state reaction [10]. The use of triblock co-polymers (P123 and F127) and charged templates (CTAB) as the structure directing agents led to the formation of mesoporous phases with BET surface area as high as 300 m^2 g^{-1} and unimodal pore sizes in the range of 2 to 15 nm. Hydrothermal treatment of the gels at 180-200^oC and calcination at 320^oC led to the formation of mesoporous nanocrystalline gallium oxide hollow spheres with an average size of 4-6 μm. The nitrogen adsorption-desorption isotherms indicated that these micron size spheres had ordered mesoporous structure with the BET surface area of 150 m^2 g^{-1} and uniform pore size in the range of 4-14 nm.

Experimental:

Gallium (III) nitrate hydrate (99.99 % -Ga) (Strem Chemicals) was used as the inorganic precursor. Hexadecyltrimethyl-ammonium bromide (CTAB, 99 %) (Sigma), Pluronic P123 (BASF) and F127 (BASF) were used as structure directing agents (SDA). For the sol-gel synthesis, ethanol (~99 % Sigma) and 1-butanol (~99 % Sigma-Aldrich) were used as the organic solvents. An aqueous solution of gallium nitrate hydrate was reacted with the structure directing agent solutions under mild synthesis conditions in order to obtain mesostructured Ga_2O_3 phases. In a typical synthesis, the inorganic precursor and SDA were separately dissolved in the organic solvent (ethanol or 1-butanol). The solutions were mixed together and vigorously stirred for 30 min and the temperature was maintained constant at 40^oC. Upon homogeneous mixing the gel was transferred to temperature-humidity chamber (set at desired conditions) and was left for 48 h, then completely dried at 60^oC and calcined at 320 or 350^oC. Alternatively, the sol-gel solution was placed in autoclaves and kept for hydrothermal treatment that led to the formation of mesoporous hollow spheres of Ga_2O_3. The resulting Ga_2O_3 phases were characterized by BET, N_2 adsorption-desorption isotherm, pore size distribution, SEM, XRD, and TEM.

Results and Discussion:

Conventional synthesis approaches have been employed in the past to obtain mesoporous gallium oxide [1, 2, 6-8]. However, these mesophases display poor crystallinity, limited thermal stability, or low specific surface areas. EISA is an emerging synthetic approach to design technologically relevant and functional oxides. We have employed this technique to overcome these limitations. EISA eliminates the strong electrostatic interactions at the inorganic-organic interface by directing the synthesis via weak hydrogen bonding interactions (when using non-ionic surfactants and thereby improving the thermal stability of the final mesostructure [11]. The resulting mesophases are thermally treated in order to stabilize the inorganic framework by removing the SDA. The nitrogen adsorption-desorption isotherms and pore size distributions were performed on samples calcined at 320^{o}, 350^{o} and 380^{o}C. The samples calcined at 320^{o}C exhibited relatively high specific surface area (~300m^{2}/g) with an average unimodal pore size distribution in the 2-15 nm range as shown in the Table 1. In case of gallium oxide, which has a high molecular mass, a surface area of ~300 m^{2}/g can be considered relatively large. Alternatively, the solution gel was placed in autoclaves for hydrothermal treatment. The temperature range of 150-220^{o}C was employed for the hydrothermal treatment that resulted in the formation of precipitates. Calcination of these precipitates led to the formation of mesoporous nanocrystalline gallium oxide spheres that were characterized by smooth surfaces and uniform size as shown in Figure 1. The size of the spherical particles increased (1.8 μm at 150^{o}C to 6.5 μm at 200^{o}C) along with the hydrothermal temperature. These mesophases show relatively high specific surface area and unimodal pore size distribution as shown in Table 1. It was observed that the pore diameter increased as the hydrothermal temperature increased, while there was a decrease in the surface area.

Table 1. General synthesis conditions and textural properties of the mesoporous nanocrystalline Ga_2O_3 obtained from EISA and Hydrothermal Treatment.

Method	Surfactant/Calcination temperature		General conditions		BET Surface area (m^2/g)	Pore diameter (nm)
			T (^oC)	RH (%)		
EISA*	CTAB	320^{o}C	30	65	298	1.9
	F127	320^{o}C	35	85	187	3.2
	P123	320^{o}C	30	65	152	4.3
			Hydrothermal Temperature (^oC)			
HT**	F127	320^{o}C	180		173	4.6
	F127	320^{o}C	200		143	8.3
	F127	320^{o}C	220		121	9.7

*EISA = Evaporation-Induced Self-Assembly
**HT = Hydrothermal Treatment

The nitrogen adsorption-desorption isotherms and pore size distributions performed on these mesoporous gallium oxide phases synthesized employing CTAB, P123, and F127, after calcination at 320^{o}C and 350^{o}C are shown in Figure 2. Higher calcination temperature led to the collapse of the mesoporous structure. The shape of the isotherm and the hysteresis loop at high relative pressure indicated that the resultant materials were mesoporous [8, 12]. The sample synthesized with F127 as shown in Figure 2A, shows a type IV isotherm representative of mesoporous solids with H2 hysteresis loop [13]. It shows a specific surface area of ~152 m^2/g with average unimodal pore diameter of ~5.2 nm. The nitrogen adsorption-desorption isotherm showing type IV isotherm and pore size distribution of gallium oxide phase synthesized using P123 in shown in Figure 2B. The sample shows a specific surface area of ~70 m^2/g with an average pore diameter of ~14.5 nm. The broader pore size distribution as compared to Figure 2A

suggests a decrease in the long-range order of this sample. The nitrogen adsorption-desorption isotherm showing type IV isotherm and pore size distribution of the mesophase synthesized using CTAB (Figure 2C) shows a specific surface area of ~139 m^2/g and an average pore diameter of ~4.8 nm. This confirms the mesoporous nature of gallium oxide. The high surface area, unimodal pore size distribution and nanocrystalline nature, are desirable properties for potential applications in heterogeneous catalysis [8].

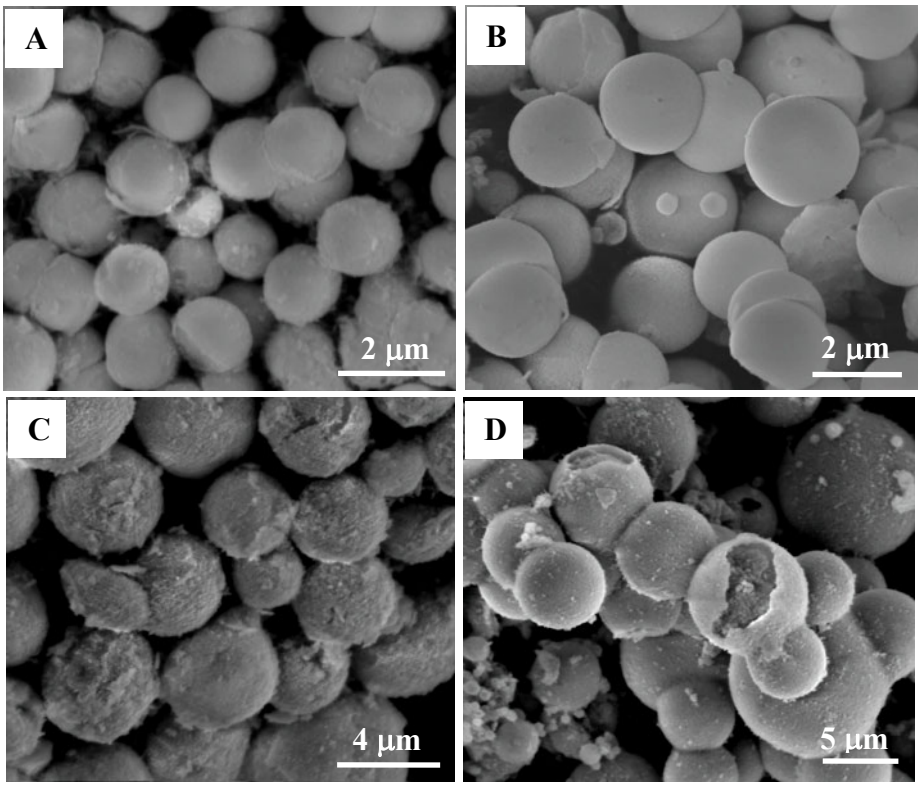

Figure 1. SEM images of mesoporous Ga_2O_3 phases with increasing size of the crystalswith respect to the Hydrothermal Temperature (A) 1.8 μm at 150°C, (B) 2.2 μm at 180°C , (C) 4.5 μm, and (D) 6.5 μm at 200°C.

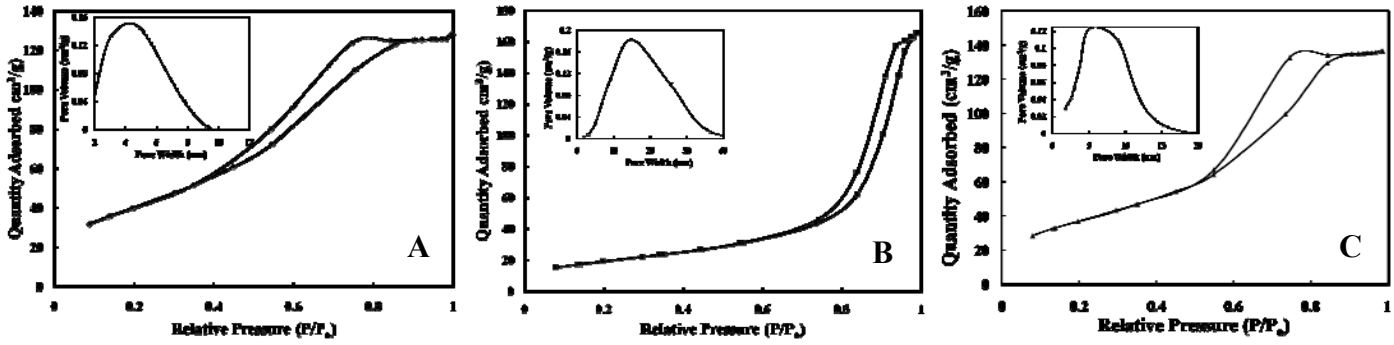

Figure 2. Nitrogen adsorption-desorption isotherms and pore size distribution of mesoporous Ga_2O_3 phases synthesized using (A) F127, (B) P123, (C) CTAB.

The mesoscopic order of the metal oxide mesophase was confirmed by XRD. The X-ray diffraction pattern of the gallium oxide phase synthesized using triblock copolymer (F127) is shown in Figure 3. The single broad low 2θ peak (Fig. 3A) at a *d*-spacing of 42.8 Å suggests the formation of a wormhole type mesostructure. Upon calcination at 320, 350 and 380^{o}C the amorphous walls of the as-synthesized mesophase crystallized [3]. The strong reflections observed at d-spacing 4.7, 2.5, 2.02, 1.6, and 1.5 Å corresponding to the (111), (311), (400), (333), and (440) planes respectively. These reflections closely resemble the cubic spinel-type structure of γ-alumina [10]. These strong reflections reveal the high crystallinity of the sample.

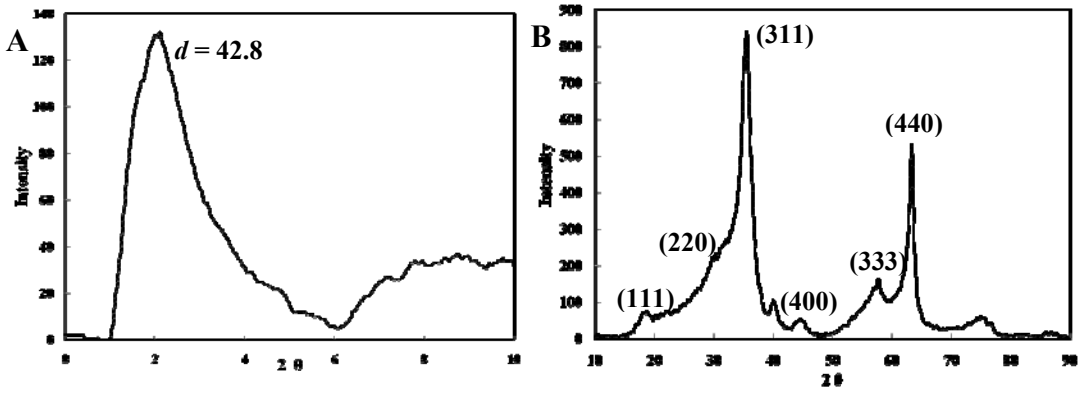

Figure 3. (A, B) X-ray diffraction pattern of the mesostructured Gallia synthesized using triblock copolymer, indicating a cubic spinel-type structure.

Conclusions:

During the last decade, EISA has emerged as a powerful synthetic route to prepare ordered mesoporous phases. In this work, we reported the successful synthesis of thermally stable mesoporous gallium oxide phases. The formation of the mesophases was confirmed by the nitrogen adsorption-desorption isotherms, XRD, and SEM. These mesoporous phases displayed unimodal pore size distribution in the 2 to 15 nm range and relatively high specific surface areas up to 300 m^2/g. Hydrothermal treatment of the as-synthesized gel led to the formation of nanocrystalline mesostructured gallium oxide spheres with uniform size in the range of 1.8 to 6.5 μm and relatively high specific surface areas (~150 m^2/g).

References

1. M. Yada, M. Ohya, M. Machida and T. Kijima, *Langmuir* **2000**, 16, 4752.
2. X. Sun and Y. Li, *Angew. Chem. Int. Ed.* **2004**, 43, 3827.
3. K. Nakagawa, C. Kajita, Y. Idle, M. Okamura, S. Kato, H. Kasuya, N. Ikenaga, T. Suzuki, *Catal. Lett.* **2000**, 64, 215.
4. K. Shimizu, A. Satsuma, T. Hattori, *Appl. Catal. B* **1998**, 16, 319.
5. K. Bethke, M. Kung, B. Yang, M. Shah, D. Alt, C. Li, H. Kung, *Catal. Today* **1995**, 26, 169.
6. P. Michorczyk and J. Ogonowski, *Appl. Catal. A: General,* **2003**, 251, 425.
7. M. Yada, H. Takenaka, M. Machida and T. Kijima, *J. Chem. Soc. Dalton Trans.* **1998**, 1547.
8. C. O. Areán, A. L. Bellan, M. P. Mentruit, M. R. Delgado, G. T. Palomino, *Microporous and Mesoporous Materials* **2000**, 40, 35.
9. (a) Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Reiker, and C. J. Brinker, Nature, **1999**, 398, 223; (b) C. J. Brinker, Y. Lu, A. Sellinger, and H. Fan, *Adv. Mater.*, **2004**, 14, 309.
10. M. A. Carreon*, V.V. Guliants, L. Y*uan, A. R. Hughett, A. Dozier, G. A. Seisenbaeva and V. G. Kessler, *Eur. J. Inorg. Chem.* **2006**, 4983.
11. (a) M. A. Carreon and V. V. Guliants, *Eur. J. Inorg. Chem*., **2005**, 1, 27; (b) A. Taguchi, and F. Schuth, *Microporous Mesoporous Mater*., **2005**, 1, 77.
12. S. J. Greg and K. S. W. Sing, Adsorption Surface Area and Porosity, Academic Press, London, **1969**.
13. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierroti, J. Rouquerol, and T. Siemieniewska, *Pure Appl. Chem*., **1985**, 57, 603.