Thermally Stable Amorphous and Nanocrystalline Mesoporous Gallium Oxide Catalysts

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Introduction

Mesoporous gallium oxides and gallium-based oxides are of great interest in the field of heterogeneous catalysis. [1] Different polymorphs of Ga_2O_3 have been employed for the dehydrogenation of alkanes to alkenes [2], epoxidation of alkenes in the presence of hydrogen peroxide [3], and in aromatization of ethane in the presence of CO_2 [4]. Current synthesis methods for the preparation of gallium oxides offer limited control over structural, morphological and compositional properties, which affect negatively its catalytic performance. [4] Surfactant-assisted self-assembly represents an attractive method for the synthesis of novel transition metal oxide catalytic phases with desirable structural, compositional and morphological properties.[5] Only a few reports have been published on the successful synthesis of thermally stable mesoporous Ga_2O_3 employing surfactants as structure directing agents (SDA). [1] However the reported synthesized mesophases showed poor crystallinity and were thermally unstable above 300°C. In the present study, we report the synthesis of thermally stable mesoporous Ga_2O_3 employing, Evaporation-Induced Self-Assembly (EISA) and Self-Assembled Hydrothermal-Assisted (SAHA) approaches. These approaches eliminate the need for high synthesis temperatures commonly needed for solid-state reactions and also offer the possibility to prepare mesoporous oxides with controlled morphological, textural and structural properties.

Materials and Methods

Gallium nitrate hydrate was used as the inorganic precursor. Hexadecyltrimethyl-ammonium bromide (CTAB), Pluronics P123 and F127 were used as the structure directing agents. In a typical synthesis, an inorganic precursor-alcohol solution was mixed with the SDA solution and was homogenized for 30 min at 40°C. The resultant gel was then transferred to a temperature-humidity chamber set at desired conditions humidity and temperature (EISA). Alternatively, the gel was placed in 45 ml Teflon lined stainless steel autoclave and heated under autogenous pressure in a static condition in conventional oven at 150°C-220°C for 20 h. The resulting precipitates were separated by centrifugation and dried overnight at 60°C.(SAHA) Calcination led to the formation of thermally stable mesoporous gallium oxide phases. The morphology and crystal size of gallium oxide mesophases were analyzed with FE-SEM (FEI Nova 600), XRD patterns were collected on Brukar D8 Discover diffractometer, N_2 adsorptin-desorption BET surface area were determined using Micromeritics Tristar-3000 porosimeter and the TEM images were taken on Technai F20 FEI TEM.

Results and Discussion

EISA produced amorphous mesoporous gallium oxide phases that displayed unimodal pore size distribution in the 2-15 nm range and relatively high specific surface areas up to ~300 m^2/g. For many structure-sensitive applications, such as in heterogeneous catalysis, it is highly desirable to have a well-defined crystalline phase. In this respect, SAHA approach was employed to prepare nanocrystalline mesoporous gallium oxide phases. This approach led to the formation of nanocrystalline mesoporous gallium oxide hollow spheres, with cubic-spinel type structure and surface area sas high as 221 m^2/g.

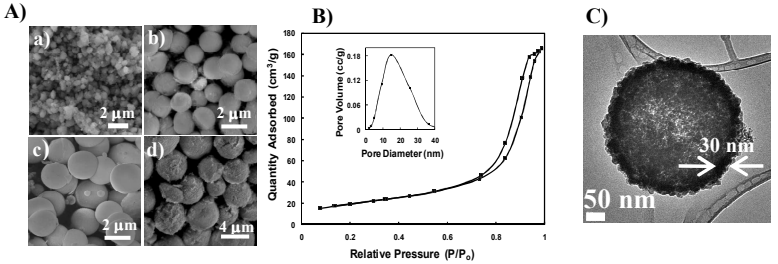

Figure 1. A) SEM images of mesoporous Ga_2O_3 synthesized by SAHA, B) N_2 adsorption-desorption isotherm and pore size distribution of mesoporous Ga_2O_3, and C) TEM image of mesoporous Ga_2O_3 hollow sphere showing cubic-spinel type nanocrystals.

The average size of the spheres was successfully adjusted in the 0.3-6.5 µm range by controlling the hydrothermal temperature between 150°C-200°C and employing ethylene glycol as an additive as seen in Figure 1A. The N_2 adsorption-desorption isotherm shows the type IV isotherm, typical of mesoporous materials [5] with unimodal pore size. These hollow spheres have a shell thickness of about 30 nm and the surface of the particles is covered with ~ 14 nm nanocrystals as shown in Figure 1C. These mesophases displayed cubic-spinel type structure as confirmed by XRD (not shown here). These novel mesophases will be tested in the oxidative dehydrogenation of propane.

Significance

The synthesized novel gallium oxide mesoporous phases are particularly promising for catalytic applications due to its high surface areas, tunability of pore sizes, and wall structure (amorphous or nanocrystalline) nature.

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