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Short Communication

Ordered mesoporous Ga_2O_3 and Ga_2O_3–Al_2O_3 prepared by nanocasting as effective catalysts for propane dehydrogenation in the presence of CO_2

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ABSTRACT

Thermally stable mesoporous gallium and gallium–aluminum (atomic ratio of Ga/Al = 4/1 and 1/4) oxides with controlled textural and structural properties were prepared by means of the nanocasting approach. All materials have uniform micron-sized particles, with a quite narrow pore-size distribution centered in the range of 6.2–6.5 nm and specific surface areas as high as 231–322 $m^2 \cdot g^{-1}$. Pure mesoporous gallium and gallium–aluminum (Ga/Al = 4:1) oxides exhibit a promising catalytic performance in the dehydrogenation of propane to propene in the presence of CO_2 (DHP-CO_2). Over the most active materials, during 4 h on stream at 823 K, propene was produced with the yield of 10–18% and high selectivity of 91–95%. Moreover, pure mesoporous gallium oxide exerted a higher resistance on deactivation during the DHP-CO_2 process in comparison with gallium oxide prepared without a hard template.

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1. Introduction

The synthesis of ordered mesoporous inorganic materials has attracted a lot of scientific interest due to their uniform mesopore sizes, high specific surface areas and ease of surface functionalization, which are features important in catalytic applications. A cooperative assembly of inorganic precursors with organic surfactants (soft templates) by sol–gel method is the most widely applied approach to mesoporous solid preparation. This soft templating synthesis method is useful especially in the case of obtaining various families of siliceous materials (e.g. MCM, SBA). However, it is not suitable for the preparation of non-siliceous materials because the hydrolysis and polymerization of transition-metal alkoxides are harder to control compared to silica alkoxides [1]. As a result, final solids have poor mesopore structure and low thermal stability after removal of templating agent.

The development of the nanocasting technique opened a new way for the synthesis of ordered mesoporous inorganic materials. In this method, a well ordered mesopore structure of the matrix, typically siliceous (e.g. SBA-15, KIT-6) or carbonaceous (e.g. CMK-3, OMC) material is filled with a precursor, which is then converted into suitable inorganic materials by thermal treatment and removal of hard template. Up to now, many different inorganic materials have been successfully prepared by nanocasting. Preparation procedures, physicochemical properties and possible applications of nanoreplicas have been discussed more precisely in several reviews [1–3].

In the last decade, several attempts at preparing ordered mesoporous Ga_2O_3 using soft templating approaches have been undertaken [4–6]. The results indicate a difficulty with the preparation of thermally stable mesophase of pure Ga_2O_3. Although using soft templates yields surfactant-Ga_2O_3 mesophase, it finally collapses during thermal treatment leading to a formation of low surface area and poorly ordered mesoporous Ga_2O_3. Similar unfavorable thermal transformation has also been observed in the case of disordered mesoporous γ-Ga_2O_3, which was converted into β-Ga_2O_3 during heating at 1073 K. This resulted in a loss of specific surface area from 120 to 40 $m^2 \cdot g^{-1}$ and in a formation of wider pores [7]. Recently, ordered mesoporous Ga_2O_3 with a high specific surface area (307 $m^2 \cdot g^{-1}$) has been prepared using nanoreplication [8]. The new method of Ga_2O_3 synthesis is very promising from the catalytic point of view because the hard template provides stable support, removed after high temperature crystallization. In the case of Ga_2O_3, the presence of hard template suppresses collapse of mesopore structure that typically occurs during gallium oxide recrystallization.

Gallium-containing materials have been widely employed as catalysts in a variety of processes including transformation of alkanes into aromatic hydrocarbons (CYCLAR process) [9], selective catalytic reduction (SCR) of NO_x in the presence of hydrocarbons as reducing agents [10,11], as well as Friedel–Crafts benzylation and acylation reactions [12]. Furthermore, bulk Ga_2O_3 (different polymorphs), Ga_2O_3 supported on TiO_2 and Ga_2O_3–Al_2O_3 spinel-type mixed oxides exhibit a promising catalytic performance in the dehydrogenation of hydrocarbons in the presence of CO_2 [13–19]. This process is considered as an alternative to the commercial dehydrogenation pathway of

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olefins production. CO, which is formed from CO_2 as a valuable by-product, can be additionally applied in chemical synthesis. It was found that in the dehydrogenation of alkanes (1) carried out over Ga-containing materials, CO_2 enhances the olefin yield and suppresses coke deposition by participation in the reverse water–gas shift (2) and Boudouard (3) reactions, respectively [13–16].

Taking into account the advantages of the nanocasting route and the promising catalytic performance of Ga-containing materials, we decided to prepare thermally stable ordered mesoporous Ga_2O_3 and Ga_2O_3–Al_2O_3 materials using CMK-3 as a hard template. The catalytic performance of the synthesized materials was investigated in the dehydrogenation of propane in the presence of CO_2 (DHP-CO_2).

2. Experimental

2.1. Preparation of materials

In a polypropylene bottle (250 cm^3), 8 g of Pluronic P123 was dissolved in a solution containing 60 g of distilled water and 120 g of 2 M HCl at 308 K. The mixture was vigorously stirred until complete dissolution of polymeric surfactant. Subsequently, 17 g of TEOS (98%, Aldrich) was added dropwise. Finally, the mixture was stirred (400 rpm) for another 20 h at 308 K and then hydrothermally treated under static conditions for 24 h at 363 K. The obtained white precipitate was filtered, dried at 333 K overnight and calcined in air by raising temperature from ambient to 823 K over 9 h period and an isothermal step at 823 K for another 12 h.

The prepared SBA-15 material was used as a hard template to the synthesis of carbon replica, CMK-3 [20]. In typical procedure, 1 g of SBA-15 was impregnated with a solution containing 5 g of water, 1.25 g of sucrose and 0.14 g of sulfuric acid. The sample was dried in two steps: at 373 K for 6 h and then at 433 K for another 6 h. The impregnation and drying procedures were repeated. In the second impregnation, a solution with 0.8 g of sucrose and 0.09 g of sulfuric acid dissolved in 3 g of water was used. Carbonization was completed in flowing N_2 by raising temperature ($1\ K \cdot min^{-1}$) up to 1073 K, at which the material was kept for another 12 h. After cooling to room temperature the carbon–silica composite was washed twice in 10% hydrofluoric solution to remove the silica template.

Mesoporous Ga_2O_3 (Ga_2O_3–m) and Ga_2O_3–Al_2O_3 (Ga_2O_3–Al_2O_3(1/4)) and Ga_2O_3–Al_2O_3(4/1) with atomic ratios of Ga/Al = 1/4 and 4/1, respectively, were obtained by the incipient wetness impregnation method according to the modified procedure reported by Roggenbuck et al. [21]. Unmodified CMK-3 carbon sieves were impregnated using an aqueous solution of metal nitrates containing 1 M of metal ions (Ga or Ga + Al). After impregnation, the materials were heated under air atmosphere to 523 K with a constant rate of $1\ K \cdot min^{-1}$ in order to decompose metal nitrates. This procedure was repeated once. In the first and second impregnations volumes of 4.0 cm^3 and 3.2 cm^3 of solution per 1 g of CMK-3 were used, respectively. Finally, the materials were calcined in two steps. First, the materials were calcined in an inert gas (N_2) atmosphere by rising temperature from ambient to 1073 K with a rate of $1\ K \cdot min^{-1}$ followed by an isothermal step at 1073 K for another 10 h. Subsequently, after cooling to room temperature the materials were heated again in a dry air flow using the same program but with the final temperature of 873 K.

The reference sample denoted as Ga_2O_3-t was prepared by the thermal decomposition of commercial $Ga(NO_3)_3$ (Fluka AG) at 873 K for 10 h.

2.2. Physicochemical and catalytic characterization

XRD patterns were collected on a Panalytical X'Pert Pro instrument operated at 40 kV and 30 mA, equipped with a Cu Kα X-ray (λ = 0.154 nm) radiation with a step size of 0.0167°.

ICP spectrometry (Perkin Elmer ELAN 6100) was applied for quantitative determination of aluminum and gallium content in the samples.

Morphology and structure of the solids were investigated by means of JEOL JSM — 7500F Field Emission Scanning Electron Microscope with the EDS (energy dispersive spectra) detection system of characteristic X-ray radiation equipped with the transmission electron microscopy detector TED. In the SEM experiments the samples were deposited on the sample holder. K575X Turbo Sputter Coater was used for coating the specimens with chromium (deposited film thickness — 20 nm). The specimens for TEM investigation were prepared by depositing a small amount of the powder samples on holey carbon films supported on copper grids.

Nitrogen adsorption–desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 instrument. Specific surface areas were calculated using the Brunauer–Emmett–Teller method within the relative pressure of $P/P_0 = 0.05$–0.15. Pore size distributions were calculated from the desorption branch using the Barrett–Joyner–Halenda method and the corrected form of the Kelvin equation proposed by Kruk et al. [22]. Total pore volumes were obtained from the volumes of nitrogen adsorbed at about $P/P_0 = 0.97$.

The samples after catalytic runs were analyzed by thermogravimetric method (TG) in flowing air ($100\ cm^3 \cdot min^{-1}$) using a SDT Q600 apparatus (TA Instruments). Ca. 5 mg of a sample was placed in a corundum crucible and heated in the temperature range of 303–1273 K at a heating rate of $20\ K \cdot min^{-1}$.

Temperature programmed desorption of ammonia (NH_3-TPD) experiments were performed in a system consisted of a quartz microreactor, a well-controlled tubular furnace and a gas chromatograph with the thermal conductivity detector (TCD). A 100 mg sample was preheated in He at 873 K for 2 h and then equilibrated with NH_3 at room temperature. Physisorbed NH_3 was removed by purging with He at 373 K for 2 h. The TPD measurement was conducted by heating the sample from 373 to 873 K at $10\ K \cdot min^{-1}$ in helium ($30\ cm^3 \cdot min^{-1}$).

The catalytic properties of mesoporous oxides were investigated in the dehydrogenation of propane in the presence of CO_2 (DHP-CO_2). This process was carried out in a flow-type quartz reactor packed with 200 mg of the catalyst (grain size 0.2–0.3 mm) in the temperature range of 773–873 K and under atmospheric pressure. The gaseous reaction mixture consisted of C_3H_8:CO_2:He = 1:5:9 (molar ratio), and the total flow rate was $30\ cm^3 \cdot min^{-1}$. The products and unreacted substrates were analyzed using an Agilent 6890N gas chromatograph (equipped with Hayesep Q and 13× molecular sieves packed columns and thermal conductivity detector), connected on-line to the reactor outlet. The conversion of propane, yield of propene and selectivity to products were calculated as described elsewhere [20].

In the selected case the prepared sample stability was investigated in the consecutive dehydrogenation, regeneration and purification cycles. DHP-CO_2 tests were carried out for 240 min at 823 K, other reaction conditions were the same as described above. After each dehydrogenation cycle the catalyst was regenerated shortly for 15 min with air at 823 K ($V_{air} = 30\ cm^3 \cdot min^{-1}$) and then purified with helium at 823 K for 5 min ($V_{He} = 30\ cm^3 \cdot min^{-1}$).

3. Results and discussion

3.1. Characterization of materials

Fig. 1 displays the XRD patterns of pure SBA-15, CMK-3 as well as Ga_2O_3–m and Ga_2O_3–Al_2O_3 mixed oxides with Ga:Al atomic ratios of 4:1 and 1:4 obtained by nanoreplication. In the 2θ range of 0.5–6.0° SBA-15 shows three diffraction lines indexed to the (100), (110) and (200) reflection characteristic for a 2D hexagonal phase (space group p6mm) [23]. The negative replica of SBA-15 (CMK-3) exhibits one intensive (100) reflection and two very weak and broad reflections, all of them are slightly shifted towards higher 2 theta values

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