Template – assisted sol – gel approach to synthesize new perspective alumina based catalysts.

V.V. Vinogradov, A.V. Vinogradov, and A.V. Agafonov

Institute of Solution Chemistry, Russian Academy of Sciences, vvv@isc-ras.ru

ABSTRACT

In this work, we have synthesized high stable mesoporous **γ-**aluminas with different pore structure. New kinds of templates were adapted to prepare alumina based catalysts with uniform and bimodal mesopore distribution with 'small' and 'large' mesopores. Preliminary catalytic tests showed high catalytic activity of synthesized samples in methanol dehydration reaction and selectivity to dimethyl ether (DME) (alternative motor fuel) comparing to conventional catalysts.

Keywords: mesoporous alumina, sol – gel synthesis, polymer – colloidal complex

1 INTRODUCTION

Aluminas are extensively used as catalyst supports due to their favorable textural properties and intrinsic acid–base characteristics. In particular, γ-alumina, which has a large surface area and a crystalline structure, is an important catalyst support in automotive and petroleum industries [1]. Mesoporous alumina with large surface area and large pore volume offers enhanced catalytic properties, and has attracted many researchers [2]. Many synthesis routes have been developed for preparing mesoporous alumina. Since the first successful synthesis of organized [3] and ordered [4] alumina using surfactant micelles as a structure – directing agent, most of the efforts have been directed towards the search of new kinds of organic templates to synthesize mesoporous crystalline alumina [5]. In this contribution, we report the synthesis of mesoporous γ–Al_2O_3 using polymer-colloid complex (PCC), polymethyl methacrylate (PMMA) nanospheres as template. Although several studies are reported on the synthesis of mesoporous crystalline aluminas, none of the reported procedures adopted facile approach using polymer-colloid complex or PMMA nanospheres. The present paper describes a highly reproducible process for the synthesis of mesoporous γ – Al_2O_3 with high surface area and a narrow pore size distribution which are an interesting and attractive materials because of its potential applications as a sorbent or catalyst support in heterogeneous catalytic reactions.

2 EXPERIMENTAL PART

2.1 Materials

Methyl methacrylate (MMA), sodium dodecyl sulfate (SDS), aluminum isopropoxide (ALISP), ammonium persulfate (APS), nitric acid (NA) were purchased from the Sigma Aldrich Company.

2.2. Synthesis

2.2.1. Preparation of aluminum precursor

The boehmite sols were prepared using Yoldas procedures by peptizing aluminum hydroxide precipitate with nitric acid [6]. In detail, 16.4 g of $Al(C_3H_7O)_3$ was added to 100 mL of deionized water and a white precipitate was formed immediately. The precipitate was peptized with 2 mL of concentrated nitric acid at 80°C under vigorous stirring for 2 h to obtain a stable boehmite sol.

2.2.2. Synthesis of the mesoporous materials with PMMA

Nanospheres of poly(methyl methacrylate) were prepared according to the following procedure [7]. SDS (1 g) was dissolved in distilled water (100 mL) with constant magnetic stirring, the solution was heated to 80°C, and then APS (0.5 g) was added. The mixture was stirred to form a homogeneous solution, and then MMA (20 ml) were injected dropwise over a period of 30 min. In the obtained solution boehmite sol was added with constant stirring and then aged for 3 h. The prepared samples were dried at 110°C overnight to form the as-synthesized samples. The mesoporous products were obtained by calcining the as-synthesized samples at 600°C for 3 h in air.

2.2.3. Synthesis of the mesoporous materials with PCC

The template solution was obtained by dissolving 4 g of the template in 10 mL of double distilled water with stirring for 15 min at 40°C. In the present study, following template was used: 50:50 mixture of polyethylenimine (PEI) M_n=10000 $(-NHCH_2CH_2-)x[-N(CH_2CH_2NH_2)CH_2CH_2-]y$ and Pluronic P123 (EO20PO70EO20, EO = ethylene oxide, PO = propylene oxide). For the synthesis of the compound, the boehmite sol was mixed with template solution with stirring at 80°C. The sample obtained with different templates were dried at 110°C overnight to form the as-synthesized samples. The mesoporous products were obtained by calcining the as-synthesized samples at 600°C for 3h in the air.

2.3. Characterization techniques

Specific surface area, pore volume, and pore size distribution of the nanosized mesoporous alumina were determined from N_2 adsorption–desorption isotherms at 77 K (Quantachrome Nova 1200). Surface area was calculated using the BET equation; pore volume and pore size distribution were calculated by the BJH method. The samples were evacuated at 300°C for 4 h prior to their analysis. The crystalline phase and crystallinity of the samples were measured by X-ray powder diffraction (XRD) analysis (Bruker D8 Advance) using Mo–Kα radiation (λ = 0.71073 Å); the samples were scanned over a 2θ range of 4–60° at a scanning rate of 2 degree per minute. The morphology was determined by transmission electron microscopy (TEM) using a LEO-906E apparatus operating at 100kV. The PMMA sol was characterized in particle size by dynamic light scattering technique using Malvern ZetaSizer Nano at 20°C with a 10mW He-Ne laser, 633 nm wavelength and 90° fixed scattering angle.

2.4. Catalytic tests

The catalytic activity of γ-Al_2O_3 in the methanol dehydration reaction was tested in a fixed-bed flow reactor system. A standard gas consisting of 11 mol% CH_3OH balanced with N_2 was fed into the reactor, in which 0.3 g of the catalyst without diluents was brought into contact with the reactant gas at a flow rate of 40 mL(STP)/min, at atmospheric pressure. The steady-state values were obtained for each temperature. The gaseous products were separated with a packed column composed of Porapak Q of gas chromatography. Prior to the test, the catalyst was first activated in situ with 30 mL/min N_2 at 300°C for 1 h. After that, the catalyst was cooled to 150°C. The effluent gas was analyzed by an on-line gas chromatography equipped with flame-ionization detector. Methanol dehydration to dimethyl ether was registered.

3 RESULTS AND DISCUSSIONS

3.1. XRD analysis

Figure 1 presents the powder XRD patterns of the calcined samples. All of the as-synthesized samples display diffraction lines of the boehmite phase (JCPDS file No. 21-1307). After calcination at 600°C, boehmite crystallites were transformed into well-crystallized γ-alumina particles (JCPDS file No. 10-0425). A calculation using Scherer equation shows γ-alumina to have crystallite size of 15.2 nm for both samples. This fact explains that adding PMMA as a template during the synthesis of alumina derived from sol-gel boehmite does not prevent the formation of crystalline structure.

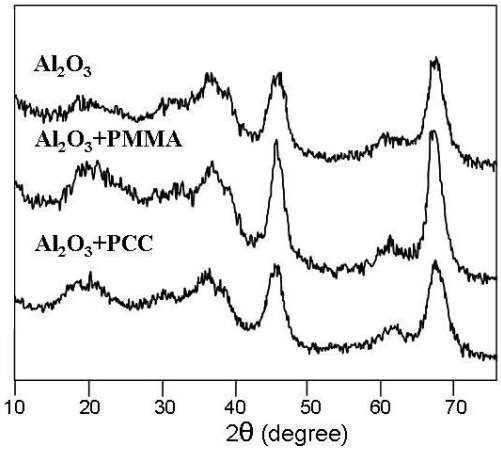

Fig.1. Results of XRD analysis.

3.2. Textural properties

According with our previous experiment the presence of template do not affect substantially the particle sizes and morphology [8]. The primary structural elements of calcined samples have roundish shape and size of about 10 nm. They coalesce into aggregates of different shapes with sizes as large as 100 nm. Figure 2 illustrates the nitrogen adsorption–desorption isotherms and pore size distributions of the calcined samples.

Pure γ-Al_2O_3 (sample 1) gives a specific surface area of about 228 m^2/g, pore volume of 0.297 cm^3/g and crystallite size of 15.2 nm, that are quite similar to the conventional γ-alumina.

The PMMA-assisted sol-gel synthesis (sample 2) leads to the destruction of ordered structure of alumina globular nanoparticles (sample 1) with formation of a new large mesopore type at 25.7 nm. Actually, applying the PMMA nanospheres during the synthesis provides an increase in surface area and pore volume up to 236m^2/g and 0.384 cm^3/g, respectively. The sample 1 shows a broad, but well-defined isotherm. A step in the adsorption isotherm curve for P/P^0 partial pressures in the range of 0.4 and 0.8 (Fig. 2) indicates the filling of the ink-bottle-type mesopores. For this sample, when the spherical particles are closely packed, pores have ink-bottle necks as shown in Fig. 2 and produce ink-bottle-type isotherm. Applying the PMMA nanospheres leads to the creation of a new peak on the pore size distribution (Fig. 2) due to the appearance of new mesopores (Dp = 25.7 nm). These larger mesopores with broader pore size distribution are in agreement with their broad hysteresis loop centered at higher relative pressures (Fig. 2) and possess bimodal mesopore distribution. The Al_2O_3-PCC sample showed the highest surface area of 333 m^2/g with the pore volume of 0.78 m^3/g. The pore size distribution curve of the sample was relatively narrow with peak at 10.5 nm. The hysteresis loop of the adsorption-desorption isotherms (Fig. 2) indicated formation of cylindrical pores. Formation of such cylindrical pores

clearly demonstrated the role of the templates in engineering the pore structure, as boehmite sol is otherwise known to form γ-Al_2O_3 with bottle–neck type pores in the absence of any structure directing template.

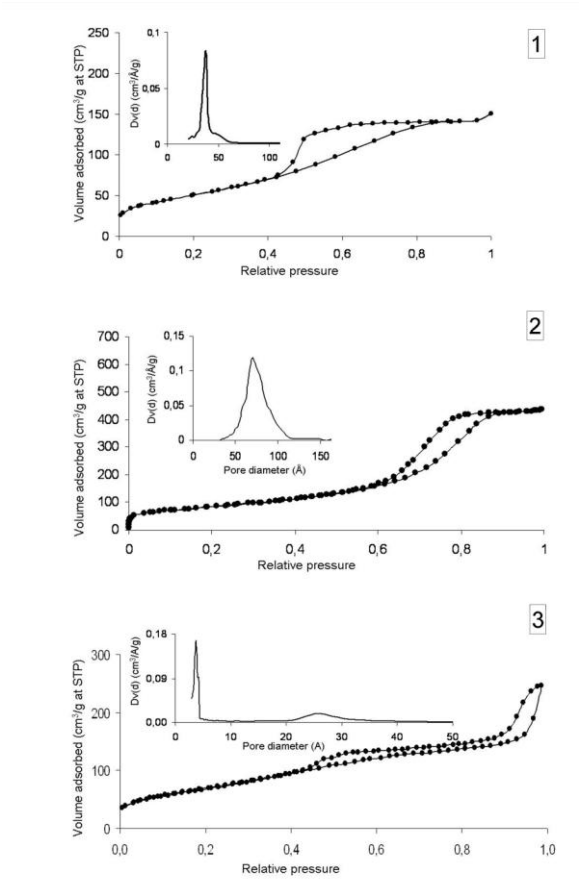

Fig.2. N_2 adsorption–desorption isotherms and pore size distribution patterns of samples 1(1), 2(3), 3(2)

The TEM images of sample 2 annealed at 600°C are displayed on Figure 3 with the corresponding electron-diffraction patterns. The TEM images confirm the presence of mesopore structure and are in a good agreement with data obtained by N_2 physisorption. The selective area of electron-diffraction pattern indicates that the mesoporous wall is crystalline with γ-Al_2O_3 phase. At the same time, amorphous phase is also present in abundance. As can be seen in Fig. 3, there are many small wormhole - like mesopores with size of 3–5 nm and spherical mesopores can be also determined. This fact confirmed the proposed mechanism of preparation of the mesoporous γ-alumina with bimodal mesopore distribution. However, when the PMMA nanospheres are used during the sol – gel process, the small mesopores become bigger and increase from 2-3 nm to 3-5 nm.

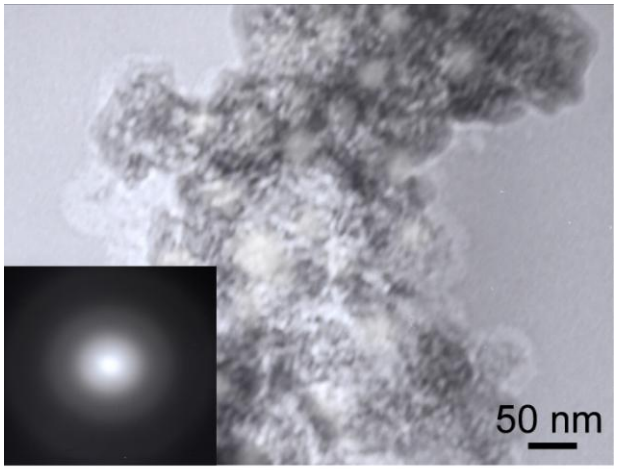

Figure.3 TEM images and of the mesoporous sample 2 and corresponding electron-diffraction patterns.

3.3. Application of catalysts to methanol catalytic dehydration

It has been known that the textural properties of mesoporous γ-aluminas have a great influence on the catalytic performance when they are used as a catalyst or support. Particularly, the presence of poor crystalline structure, high surface area and a uniform pore size distribution for methanol catalytic dehydration can often lead to an enhancement in catalytic activity [5]. In the present work, we have chosen the reaction of methanol dehydration to dimethyl ether as a model reaction for evaluating the influence of the textural properties of γ-Al_2O_3 on the catalytic performance. This reaction is a very important for obtaining dimethyl ether due to its good properties as an alternative kind of biodiesel fuel. Thus, with reference to our previous work [5], we have prepared catalysts with different conditions in order to discuss their catalytic properties.

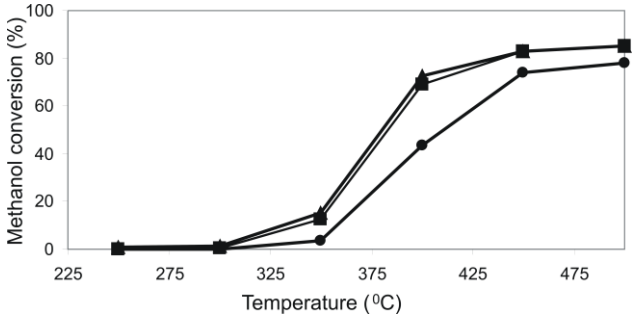

Fig.4 Methanol conversion on (●) Sample 1, (■) Sample 2 and (▲) Sample 3

Fig. 4 illustrates the methanol conversion to dimethyl ether as a function of the reaction temperature. Comparing to Sample 1 prepared without template, both Sample 2 and Sample 3 showed remarkable improvements in their catalytic activity. Up to 500^0C Maximum methanol conversion for Sample 1 achieved only 78%, while on the Sample 2 and 3 it was around 85%. Moreover, at 400^0C methanol conversion on sample 2 and 3 (~70%) increased

more drastically in comparison to sample 1 (only 44%). As we can see in Fig.6 catalytic activity of Sample 2 and 3 are very similar. On the other hand surface areas of these samples very strongly differ. This phenomenon is related with different textural features. Sample 2 prepared by template-assisted sol-gel synthesis is characterized by an unusual bimodal mesoporous structure with pore diameters of 3.8 and 25.7 nm leading to an increase in catalytic activity. Carrying out catalytic reaction on a catalyst surface is always related with transport of reaction reagents and products to an internal surface and from them. Depending on porous structure process can be limited chemical transformations or diffusion braking. Decreasing of reagent concentration from external border to the centre of a catalyst particle determines efficiency of use of porous structure.

4 CONCLUSIONS

Mesoporous γ-aluminas were prepared using two different approaches. With first approach we used PMMA nanospheres as a structure-directing agent and with second applied polymer – colloidal complex during the synthesis. The PMMA nanospheres have been prepared using an emulsion polymerization method. Spherical γ-Al_2O_3 particles prepared without template are closely packed and pores have ink-bottle necks with very narrow distribution. γ-Al_2O_3 which has been prepared with using PCC shows larger mesopores with broader pore size distribution and exhibits high parameters of surface area and pore volume. The γ-Al_2O_3 that has been prepared using the PMMA nanospheres shows bimodal mesopore distribution with pore size of 3.8 and 25.7 nm. It is shown that mesoporous γ-Al_2O_3 prepared with PMMA particles demonstrates high catalytic activity in the methanol dehydration reaction to dimethyl ether. This phenomenon is related to the unusual porous structure compared to the conventional γ-alumina samples. Obviously, applying the PMMA nanospheres as templates has a very significant effect on the microstructure and, as a result, on the catalytic properties.

5 ACKNOWLEDGEMENTS

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