



Original Research Paper

A facile synthesis strategy for structural property control of mesoporous alumina and its effect on catalysis for biodiesel production



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ABSTRACT

A facile synthesis route for the production of mesoporous alumina (MA) with tuneable structural properties including BET surface area, pore volume and pore size was systematically investigated by tailoring the amount of template P123 used in the synthesis. The general synthesis strategy was based on a sol–gel process by hydrolysis of aluminium isopropoxide associated with nonionic block copolymer (P123) as the template in a water system. The results showed that the addition of P123 played a crucial role in the synthesis process, leading to very regular variations in the surface area (146.6–261.6 m²/g), pore volume (0.164–2.152 cm³/g) and pore size (3.5–29.9 nm). MA-supported K species (MA-K) were prepared using KNO₃ as the potassium precursor and adopted as the catalysts for biodiesel production. The introduction of K species to MA caused a reduction in the BET surface area and pore volume, but gave rise to a significant increase in pore size, especially when the K species was higher than 10%. K incorporation resulted in the formation of disordered, but significantly larger mesopores. In catalysis, by introducing 20% molar fraction of K species to MA, very high yield of biodiesel was achieved (92.2%) and further increased to 94.4% with 25% K. Based on the control of structural properties of MA, a series of MA-20K catalysts with the same K loading (20%) but different structural properties were prepared by varying P123 addition and were further tested in biodiesel synthesis. Higher biodiesel yields were obtained over the MAs with higher surface area, pore volume and bigger pore size, which were attributed to the reduced mass transfer limitation in catalysis.

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1. Introduction

Since the discovery of ordered mesoporous silica materials in 1992 [1], research interest in this field has been flourishing worldwide because of the envisioned applications of these porous materials in catalysis, photoelectronics, sensors, energy conversion, adsorption, separation and biomedical sciences [2,3]. Compared to silica, alumina gained more popularity from a heterogeneous catalysis perspective for its extensive applications as industrial catalysts and catalyst supports utilised in petroleum refining, automobile exhaust emissions control, steam reforming, and numerous other chemical processes, owing to its thermal and mechanical stability as well as amphiprotic properties [4–6]. Therefore, considerable efforts have been dedicated to extending such mesostructured materials to alumina [7–11]. With mesoporosity features such as highly uniform channels, large surface area and narrow pore-size distribution, the mesostructured alumina is

envisioned to minimize the mass transfer resistance of reactants and products in and out of the catalyst particles [4,5].

Unfortunately, typical recipes for the preparation of ordered mesoporous silica do not work effectively for the synthesis of alumina analogues, due to fast hydrolysis and condensation rates of aluminium alkoxides, which often result in the formation of disordered alumina. As such, in most reported cases, disordered mesostructures with amorphous walls were obtained [7]. At present, ordered mesoporous alumina materials (MAs) are commonly synthesized by the following general pathways: (1) by adopting the nanocasting method with polymers and carbon molds as hard templates [12], (2) by solvent-deficient synthesis without the SDAs and templates [13,14], and (3) a pathway based on a modified sol–gel self-assembly process in the presence of a soft template such as a cationic, anionic, or nonionic surfactant as the structure-directing agent (SDA) [6–11,15,16]. However, the pathway (1) has long been criticized for its complexity and time-consuming synthesis process [12]. While the pore size of MA has been expanded from 7 to 37 nm [13] by using the pathway (2), the modulation was not continuous, and only particular values can be obtained due to the lack of a

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template. In 2005, Niesz et al. [17] reported the successful synthesis of ordered MA using block copolymers as the soft template for the first time, i.e. the origin of pathway (3). Since then, a significant breakthrough has been realized following this general pathway by using the (EO)₂₀(PO)₇₀(EO)₂₀ triblock copolymer (P123) as the soft template in ethanol solution. This route is called the solvent evaporation induced self-assembly (EISA). EISA can competently substitute the process of cooperative assembly of precursors and surfactant templates typically employed to afford mesoporous materials. Consequently, it enables the synthesis of ordered MA in an easy and reproducible manner and obviates the necessity to strictly control hydrolysis conditions [18]. However, there are still challenges including the interactions between metal precursors, template and other additives. Understanding of such interactions will enable us to manipulate MA with tailored structural properties especially the pore size for use in catalysis.

Of particular interest is the investigation of the impact of template P123 on MA and further to control its structural properties. Bai et al. [19] realized the control of pore size from 3.4 to 6.2 nm, pore volume from 0.2 to 0.58 cm³/g and BET surface area from 182 to 323 m²/g by using the cation–anion double hydrolysis method. Similarly, Alphonse and Faure [20] reported a dramatic pore size expansion from 4 nm to around 12 nm in a modified water system. However, to the best of our knowledge, literature reports on the pore size expansion greater than 15 nm through tailoring the usage of template P123 are scarce, although there have ever been reported for MA pore size modulation up to 37 nm following the pathway (2) [13]. In general, pore size of the order of 15 nm still limits the penetration of large molecules in catalysis reactions.

In this work, we have systematically investigated the effect of P123 on the structural properties of synthesized alumina. The pore size was found to be controllable up to as high as 29.9 nm. Moreover, as the synthesis recipe has been modified to use water instead of ethanol as the medium. This modification enabled the active component of potassium species to be introduced to the support alumina in the one-pot synthesis pathway instead of the commonly utilised post synthesis method like impregnation. The prepared materials were adopted as the solid base catalysts for biodiesel production by transesterification of canola oil with methanol. The effect of potassium loading on the structural properties of the catalysts and thus the catalytic activity of MA was investigated.

2. Experimental

2.1. Chemicals

Pluronic P123 (*M_w* = 5800, EO₂₀PO₇₀EO₂₀, EO = ethylene oxide, PO = propylene oxide) and aluminium iso-propoxide were purchased from Sigma–Aldrich. Fatty acid methyl esters, methyl myristate (C14:0), methyl palmitate (C16:0), methyl palmitoleate (C16:1), methyl stearate (C18:0), methyl oleate (C18:1), methyl linoleate (C18:2), methyl linolenate (C18:3), methyl arachidate (C20:0), methyl cis-11-eicosenonate (C20:1) and methyl behenate (C22:0) were also purchased from Sigma–Aldrich, and utilised as the reference standards for gas chromatograph (GC) analysis, while methyl nonadecanoate (C19:0) was used as the internal standard. All chemicals were used as received without further purification.

2.2. Catalysts synthesis

MA was synthesized as follows. 36 mL (2 mol) of hot water (85 °C) was quickly added to 4.08 g (20 mmol) of aluminium iso-

propoxide under vigorous stirring. The hydrolysis ratio, $h = [\text{H}_2\text{O}]/[\text{Al}]$ was 100. After 15 min, the white precipitate was peptized by adding 0.47 ml nitric acid (HNO₃, 68%, Fluka, $[\text{HNO}_3]/[\text{Al}] = 0.35$) and maintained at 85 °C for 12 h while the white suspension changed gradually to a transparent sol. The reaction flask was kept uncovered in the first 2 h to allow the evaporation of isopropanol formed during the hydrolysis. The template Pluronic P123 was added to the sol and the mixture was kept under gentle stirring for another 12 h at room temperature. Then, the xerogel was made by drying the sol in air in an oven at 70 °C for 12 h. The glassy material obtained was calcined in air at 700 °C for 4 h. The resulting MA sample was ground using a pestle and mortar into a fine powder.

In order to investigate the effect of template P123 on the structural properties of the MA synthesised, different amount of P123 was added in. The resulting materials were denoted in a general form MA-xP, where x indicate the amount of P123 added in synthesis. Specifically, for every 20 mmol of aluminium, the amount of P123 was ranged from 0 to 4 g, named as xP. For instance, MA-1P refers to an MA sample synthesised with 1 g P123 and 0.47 ml nitric acid and then calcined at 700 °C for 4 h in air. The MA-supported potassium oxide catalysts (MA-K) were prepared by the one-pot synthesis method via self-assembly of potassium precursor KNO₃ and aluminium isopropoxide [17,18]. A desired amount of KNO₃ was added in the sol together with P123 and the mixture was kept under gentle stirring for 12 h at room temperature. Otherwise, the synthesis was the same as for MA as described above. The total quantity of the metal species (20 mmol) was kept constant, and the molar ratio of K was adjusted accordingly (5%, 10%, 15%, 20%, 25%). The final samples were labelled as MA-xP-mK, where x refers to “x” g of P123 per 20 mmol of Al during the material preparation, and m denotes “m” mol% of K-species in a sample.

2.3. Materials characterization

Adsorption parameters including the BET surface area, pore volume and pore size distribution (PSD) for the samples were determined from the obtained nitrogen sorption isotherms. The isotherms were measured using a Tristar 3020 volumetric analyser (Micromeritics Co. Ltd.). Prior to a measurement, the sample was degassed under vacuum at 200 °C overnight to remove moisture and other absorbed species. The specific surface area was calculated from the adsorption data using the Brumauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.3. The PSD was derived from desorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) calculations. Pore size *D_p* means the peak positions of the distribution curves and when *D_p* reaches as high as about 20 nm with broad PSDs, these values reflect only an approximate mesopore maximum. *D_a* indicates the average pore diameter by BET. The pore volume *V_p* shows the BJH desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width.

Powder X-ray diffraction (XRD, Empyrean, PANalytical, Cu K α radiation at 40 kV, 40 mA) was used to perform wide angle X-ray scattering (WAXS) from 10° to 80° and small angle X-ray scattering (SAXS) from 0.5° to 5°. Microscope glass slides were used as supports.

Microstructure of the catalysts were imaged using scanning electron microscopy (SEM) (Zeiss) operating at 15 kV accelerating voltage. Transmission electron micrographs (TEM) were recorded with a JEM-2100 JEOL electron microscope equipped with LaB6 filament and operating at 120 kV. Samples were gently ground, dispersed in ethanol by moderate sonication and then deposited on a Cu grid (200 mesh).

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