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

Wei Wu, Zhijian Wan, Wan Chen, Hong Yang and Dongke Zhang*

Centre for Energy (M473)

The University of Western Australia

35 Stirling Highway, Crawley, WA 6009, Australia

(A manuscript offered to *Advanced Powder Technology*)

*corresponding author:

Email: Dongke.Zhang@uwa.edu.au

Phone: 61-8-6488 7600

Fax: 61-8-6488 7235

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 ($146.6 \sim 261.6 \text{ m}^2/\text{g}$), pore volume ($0.164 \sim 2.152 \text{ cm}^3/\text{g}$) and pore size ($3.5 \sim 29.9 \text{ nm}$). MA-supported K species (MA-K) were prepared using KNO_3 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.

Keywords: biodiesel synthesis; catalysis; mesoporous alumina; P123; structural properties

1 **Introduction**

2 Since the discovery of ordered mesoporous silica materials in 1992 [1], research interest in
3 this field has been flourishing worldwide because of the envisioned applications of these
4 porous materials in catalysis, photoelectronics, sensors, energy conversion, adsorption,
5 separation and biomedical sciences [2, 3]. Compared to silica, alumina gained more
6 popularity from a heterogeneous catalysis perspective for its extensive applications as
7 industrial catalysts and catalyst supports utilised in petroleum refining, automobile exhaust
8 emissions control, steam reforming, and numerous other chemical processes, owing to its
9 thermal and mechanical stability as well as amphiprotic properties [4-6]. Therefore,
10 considerable efforts have been dedicated to extending such mesostructured materials to
11 alumina [7-11]. With mesoporosity features such as highly uniform channels, large surface
12 area and narrow pore-size distribution, the mesostructured alumina is envisaged to minimize
13 the mass transfer resistance of reactants and products in and out of the catalyst particles [4, 5].
14 Unfortunately, typical recipes for the preparation of ordered mesoporous silica do not work
15 effectively for the synthesis of alumina analogues, due to fast hydrolysis and condensation
16 rates of aluminum alkoxides, which often result in the formation of disordered alumina. As
17 such, in most reported cases, disordered mesostructures with amorphous walls were obtained
18 [7]. At present, ordered mesoporous alumina materials (MAs) are commonly synthesized by
19 the following general pathways: (1) by adopting the nanocasting method with polymers and
20 carbon molds as hard templates [12], (2) by solvent-deficient synthesis without the SDAs and
21 templates [13, 14], and (3) a pathway based on a modified sol-gel self-assembly process in the
22 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 template. In 2005, Niesz [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 realised 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 utilized 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.

Experimental

Chemicals

Pluronic P123 ($M_{av} = 5800$, 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.

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 isopropoxide 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 (HNO_3 , 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 synthesized 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 KNO_3 and aluminum isopropoxide [17,18]. A desired amount of KNO_3 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.

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).

Biodiesel synthesis

Biodiesel synthesis was carried out in a 50 ml round-bottom flask equipped with a condenser and a magnetic stirrer. All transesterification reaction runs were carried out under identical conditions of 5 g canola oil, 0.1 g catalyst, 15:1 molar ratio of methanol to oil at 70°C under stirring. After reaction, the liquid was allowed to cool naturally to room temperature and subjected to centrifuging at 5,000 rpm for 20 min to enhance phase separation. Two liquid phases were formed after separation, with the crude methyl esters (ME) phase at the top and glycerol at the bottom.

The fatty acid compositions of the used canola oil are summarised in Table 1. It was composed of 6.5% saturated fatty acids and 93.5% unsaturated fatty acids, dominated by the one double bond oleic acid C18:1 (63.9%).

The composition of ME produced was analysed using an Agilent 7890 GC equipped with a flame ionization detector (FID) and a J&W (Folsom, CA, USA) DB-Wax capillary column (30 m×0.25mm I.D., fused-silica column coated with 0.25 µm polyethylene glycol film). The injector and detector temperatures were set at 250 °C. The oven was heated from 60°C to 210°C at a rate of 20°C/ min, held for 9 minutes. MEs were identified by comparing the

retention times with those of a mixture of standard MEs while the content was calculated based on the internal standard method using methyl nonadecanoate as the reference. The yield of biodiesel was calculated according to:

$$Yield(\%) = \frac{M_1 * f}{M_2} * 100\% \quad (1)$$

where M_1 is the mass of the top phase obtained after phase separation, f is the percentage of ME content in the top phase obtained by the GC analysis, and M_2 is the mass of canola oil used.

Results and discussion

The effect of P123 on MA

Effects of template P123 addition on the nitrogen sorption isotherms and the corresponding pore size distributions of representative MA samples are shown in Figure 1 (A and B) while the full set of data is detailed in Figure S1 (A and B) of Supporting Information. The structural properties derived from these isotherms, including BET surface area, pore volume and pore size are summarized in Table 2. In all cases, the isotherms displayed are Type IV with H1 hysteresis loops, suggesting the presence of cylindrical mesopores. A very clear shift of the capillary condensation steps to greater relative pressures was observed, indicating a substantial increase of the average pore size. ~~Moreover, the increasingly sharp steepness of the capillary condensation steps also indicated a higher degree of mesopore uniformity from MA to MA-4P [20].~~ In the corresponding PSD curves shown in Figure 1B, the isotherms with steep condensation steps (e.g., MA-3P) can still represent very narrow pore size distributions. When it comes to MA-4P, however, although the peak value of the PSD reached 29.9 nm, the

1 PSD curve became broad.

2 As can be seen, the structural properties of MA were highly dependent on the amount of P123
3 addition in the synthesis. With increased P123 up to 4 g, the BET surface area (from 146.6
4 m^2/g to 261.6 m^2/g), pore volume V_p (0.164 cm^3/g to 2.152 cm^3/g), average pore size D_a (3.6
5 nm to 24.3 nm) and the peak value of PSD curves D_p (3.5 to 29.9 nm) increased gradually.

6 More impressively, a ~~sufficiently~~relatively narrow PSD was maintained even when the pore
7 size was increased from 3.5 nm (MA) to as high as 23 nm (MA-3P).

8 Indeed, the addition of P123 can induce the crystal growth along specific directions following
9 a SIFF mechanism [21] or a layer-by-layer self-assembly mechanism [22]. Therefore, the
10 addition of a small amount of P123 can promote the crystal growth. However, because of
11 micellization of the tri-block copolymer surfactant, continuous increase of P123 addition will
12 lead to an increase in solution viscosity, thus reduce the mobility of nanoparticles and hinder
13 the subsequent self-assembly process [23]. Consequently with increasing amount of P123
14 used in the synthesis, especially when the amount reached 2 g and above, the PSD became
15 progressively broader.

16 The SAXS patterns shown in Figure 2 (A ~~and~~& B) confirm the existence of ordered
17 mesopores in the MA samples including MA-0.25P, MA-0.5P and MA-0.75P. It is
18 well-known that the diffraction peaks at low angles provide the evidence for highly ordered
19 mesoporosity, and the single diffraction line is characteristic of mesoporous structures with no
20 long-range order in the pore arrangement [24]. However, no such peaks were observed in the
21 SAXS spectra for the remaining samples, such as MA-1P and MA, indicating the existence of
22 disordered mesoporosity. The SAXS results indicate that only the addition of P123 in a

specific range can bestow MA with highly ordered mesoporosity.

Typical SEM images of MA (A), MA-1P (B) MA-4P (C) [and MA-1P-20K \(D\)](#) are shown in

Figure 3. For the former three MA-xP samples, with increasing P123, the small particles

became increasingly larger and bumpier especially for MA-4P. ~~While for MA-1P-20K,~~

~~after doping 20% mol/mol of K, the surface became flat and smooth, quite different from~~

~~those of the MA-xP samples without K incorporation. Figure 3 E~H~~ display TEM images of

MA-0.25P, MA-0.75P, MA-1P and MA-1P-20K, respectively. The TEM images for the first

three samples without K show similar wormhole-like appearance of MA pores, with no

significant ordering observed in the pore arrangement, ~~which is in good agreement with the~~

~~absence of high order peaks in the small angle X ray diffraction patterns in Figure 2.~~

Combining with the nitrogen sorption analysis, the wormlike mesopores should have good

interconnection in order to achieve the high surface area and pore volume observed. For the

[MA-1P-20K \(H\)](#), however, the TEM microstructure was very different from the others; here

no randomly arranged pores and small particles could be observed. From the SEM and TEM

images of MA-1P-20K, it can be seen that the 20K doping caused significant changes to the

microstructure of MA. The subsequent nitrogen sorption analysis shows that such structural

change resulted in a decrease of surface area and pore volume, but an increase in pore

diameter.

MA supported potassium by the one-pot pathway

The effect of K loading on both the structural properties and catalytic activity of MA was

investigated. [The nitrogen sorption isotherms and the corresponding pore size distributions of](#)

[the typical MA-1P-mK samples are shown in Figure 4 \(A and B\) with the full set of data](#)

detailed in Figure S2 (A and B) of Supporting Information. As clearly shown in Table 3 and Figure 4 (A&B), the introduction of K species leads to a continuous reduction of the BET surface area, but a progressive increase in the pore size, especially when the K loading is higher than 10%. For the pore volume, however, the results show that if the loading ratio of K is no more than 10%, a slight increase in pore volume can be observed. However, further increase of the K ratio over 10% will result in substantial decrease of pore volume. The excessive K loading results in the formation of disordered mesopores and broader PSD. Up to 10% K species loading, the samples display uniformity and uniform mesopores.

The catalytic activity of MA-K in transesterification of canola oil with methanol is highly dependent on the K loading. The yield of biodiesel reached 92.2% by using the catalyst MA-1P-20K and further increased to 94.4% by MA-1P-25K (Table 3). The methyl ester compositions in the resulting biodiesel from the GC analysis are shown in Table 5. It is interesting to note that the concentrations of methyl esters the biodiesel obtained corresponded to the fatty acid compositions of the canola oil shown in Table 1, indicating that the catalysts were not selective and did not favour any particular fatty acids in this catalytic transesterification process. The structural properties of catalysts only affected the yield, not the composition, of the biodiesel.

Figure 5 shows the wide-angle XRD patterns for the K-containing alumina samples MA-1P-mKs calcined at 700°C. The alumina is in γ phase (JCPDS Card No. 10-0425). The patterns show two main sharp peaks at $2\theta = 45.8$ and 66.6° . As the molar fraction of K increases from 5K to 20K, the gradually reduced peak intensity and peak broadening were observed, suggesting the reduction in crystallinity. Besides, there was no any form of K

compounds can be found. But for MA-1P-25K, except for γ -Al₂O₃, KAl(CO₃)₂(OH)₂ was identified, most likely owing to the complex reactions of K₂O generated from KNO₃ decomposition with Al₂O₃, CO₂, O₂ and H₂O exposed in the open air.

Effect of structural properties on catalytic activities in biodiesel synthesis

A series of MA-xP-20K catalysts were prepared to investigate the effect of the structural properties of MA on the catalytic activity in biodiesel synthesis. Based on the analysis discussed above, different amounts of P123 were used in the synthesis to control the structural properties of the catalyst. The measured isotherms and the corresponding structural parameters are summarised in Figure 6 (A and B) and Table 4, respectively. As can be seen from Table 4, compared with MA-xP in Table 2, the addition of 20% K species had a marked effect on the structural parameters obtained; it dramatically reduced the BET surface area and pore volume, while increased the pore width. In the nitrogen sorption isotherms shown in Figure 6A and BJH pore size distribution shown in Figure 6B, with increased addition of P123 from 0 to 1 g, the higher adsorption volume indicates a greater pore volume and the shift of the hysteresis loops to greater relative pressures illustrates the expansion of the pore width. A strong correlation between the structural properties of MA-xP-20K samples and their catalytic activities in biodiesel synthesis within 2 h reaction were observed. In this case, under the same reaction conditions, the yield of biodiesel increased from only 29.1% over the catalyst MA-20K to 78.9% of MA-0.25P-20K and further achieved 86.8% by using MA-1P-20K (Table 4). The methyl ester compositions of the biodiesel obtained are also shown in Table 5. These results show that a higher surface area, greater pore volume and pore size can greatly reduce the mass transfer in the catalysts, leading to freer mass transfer of the

reactants and reaction products and bigger surface area for adsorption and desorption in catalysis, thus achieving much higher yields.

Conclusions

Mesoporous alumina (MA) with tuneable structural properties including the BET surface area, pore volume and pore size was successfully synthesized in this study by tailoring the amount of template P123 used in the synthesis. By varying template P123 to control the structural properties and incorporating K as the active phase, very high biodiesel yields were obtained.

The main conclusions can be drawn as follows:

1. In the MA synthesis, increasing the amount of template P123 led to an increase in the BET surface area, pore volume and pore size substantially, thus achieving the control of structural properties of MA in the range of $146.6 \sim 261.6 \text{ m}^2/\text{g}$, $0.164 \sim 2.152 \text{ cm}^3/\text{g}$ and $3.5 \sim 29.9 \text{ nm}$ for surface area, pore volume and pore size, respectively.

2. K species was dispersed into MA to obtain a mesoporous material (MA-K) through the one-pot synthesis pathway via self-assembly of potassium precursor KNO_3 and aluminum isopropoxide. While the K incorporation has reduced the BET surface area and pore volume of the synthesized MA-K catalysts, it has increased the pore size significantly. When applied in catalysis, by introducing 20% molar fraction of K species to MA, a very high yield of biodiesel of 92.2% was achieved and further increased to 94.4% with 25% K.

3. Higher surface area, pore volume and greater pore size reduced the mass transfer limitation in catalysis, thus leading to the higher biodiesel yields over the MA-20K series catalysts with the same K loading but different structural properties by tailoring the usage of P123 in the

1 synthesis.

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References

1. CT Kresge, M.L., WJ Roth, JC Vartuli, JS. Beck, Ordered mesoporous molecular sieves synthesised by a liquid-crystal template mechanism. *Nature*, 1992. 359: p. 710-712.
2. Meynen, V., P. Cool, and E.F. Vansant, Verified syntheses of mesoporous materials. *Microporous and Mesoporous Materials*, 2009. 125(3): p. 170-223.
3. Martín-Aranda, R.M. and J. Čejka, Recent Advances in Catalysis Over Mesoporous Molecular Sieves. *Topics in Catalysis*, 2009. 53(3-4): p. 141-153.
4. Ren, Y., Z. Ma, and P.G. Bruce, Ordered mesoporous metal oxides: synthesis and applications. *Chemical Society Reviews*, 2012. 41(14): p. 4909-27.
5. Trueba, M. and S.P. Trasatti, γ -Alumina as a Support for Catalysts: A Review of Fundamental Aspects. *European Journal of Inorganic Chemistry*, 2005. 2005(17): p. 3393-3403.
6. Čejka, J., Organized mesoporous alumina: synthesis, structure and potential in catalysis. *Applied Catalysis A: General*, 2003. 254(2): p. 327-338.
7. Maekawa, H., Size-dependent ionic conductivity observed for ordered mesoporous alumina-LiI composite. *Solid State Ionics*, 2004. 175(1-4): p. 281-285.
8. Kim, P., et al., Synthesis and characterization of mesoporous alumina with nickel incorporated for use in the partial oxidation of methane into synthesis gas. *Applied Catalysis A: General*, 2004. 272(1-2): p. 157-166.
9. Paul, M., et al., New mesoporous magnesium–aluminum mixed oxide and its catalytic activity in liquid phase Baeyer–Villiger oxidation reaction. *Chemical Engineering*

- Science, 2012. 71: p. 564-572.
10. Xu, B., et al., Synthesis of mesoporous alumina with highly thermal stability using glucose template in aqueous system. *Microporous and Mesoporous Materials*, 2006. 91(1-3): p. 293-295.
11. C Márquez - Alvarez, N.Ž., J Pérez - Pariente and Jiří Čejkab, Synthesis, characterization and catalytic applications of organized mesoporous aluminas. *Catalysis Reviews Science and Engineering*, 2008. 50(2): p. 222-286.
12. Wu, Z., et al., Ordered mesoporous crystalline γ -Al₂O₃ with variable architecture and porosity from a single hard template. *J. Am. Chem. Soc.*, 2010. 132(34): p. 12042-12050.
13. Huang, B., C.H. Bartholomew, and B.F. Woodfield, Facile structure-controlled synthesis of mesoporous γ -alumina: Effects of alcohols in precursor formation and calcination. *Microporous and Mesoporous Materials*, 2013. 177: p. 37-46.
14. Huang, B., et al., Facile solvent-deficient synthesis of mesoporous γ -alumina with controlled pore structures. *Microporous and Mesoporous Materials*, 2013. 165: p. 70-78.
15. Kondo, J. and K. Domen, Crystallization of Mesoporous Metal Oxides. *Chemistry of Materials*, 2008. 20(3): p. 835-847.
16. Ghosh, S., M.K. Naskar, and T. Troczynski, Understanding the Role of Triblock Copolymers for the Synthesis of Mesoporous Alumina, and Its Adsorption Efficiency for Congo Red. *Journal of the American Ceramic Society*, 2014. 97(1): p. 100-106.
17. Niesz, K., P. Yang, and G.A. Somorjai, Sol-gel synthesis of ordered mesoporous

alumina. Chem Commun (Camb), 2005(15): p. 1986-7.

18. Yuan, Q., et al., Facile synthesis for ordered mesoporous γ -aluminas with high thermal stability. J. Am. Chem. Soc., 2008. 130(11): p. 3465-3472.

19. Bai, P., et al., Cation–anion double hydrolysis derived mesoporous γ -Al₂O₃ as an environmentally friendly and efficient aldol reaction catalyst. Journal of Materials Chemistry, 2009. 19(11): p. 1554.

20. Alphonse, P. and B. Faure, Synthesis of highly porous alumina-based materials. Microporous and Mesoporous Materials, 2013. 181: p. 23-28.

21. Peng Bai, F.S., Pingping Wu, Likui Wang, Fang Yin Lee, Lu Lv, Zi-feng Yan, and X. S. Zhao, Copolymer-Controlled Homogeneous Precipitation for the Synthesis of Porous Microfibers of Alumina. Langmuir, 2007. 23(8): p. 4599–4605.

22. H. Y. Zhu, J.D.R., and J. C. Barry, γ -Alumina Nanofibers Prepared from Aluminum Hydrate with Poly(ethylene oxide) Surfactant. Chemistry of Materials, 2002. 14(5): p. 2086–2093.

23. Peng Bai, P.W., Zifeng Yan, Jinkai Zhou, X. S Zhao, Self-Assembly of Clewlike ZnO Superstructures in the Presence of Copolymer. The Journal of Physical Chemistry C, 2007. 111(27): p. 9729–9733.

24. Lin-Bing Sun, W.-H.T., and Xiao-Qin Liu, Magnesia-Incorporated Mesoporous Alumina with Crystalline Frameworks: A Solid Strong Base Derived from Direct Synthesis. J. Phys. Chem. C, 2009. 113(44): p. 19172–19178.

Figure captions:

- Figure 1 Nitrogen sorption isotherms (A) and PSD (B) of typical MA-xP samples. Note that, the remaining curves for MA-0.25P, MA-0.75P, MA-1.5P, MA-2P are represented in sSupporting information Figure S1.
- Figure 2 Small angle x-ray scattering (SAXS) from 0.5° to 5° of typical MA-xP samples
- Figure 3 SEM images of the as-made aluminas: MA (A), MA-1P (B), MA-4P (C) and MA-1P-20K (D). The scale bars are 100 nm. E ~ H are the TEM images of MA-0.25P, MA-0.75P, MA-1P and MA-1P-20K, respectively.
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- Figure 6 Nitrogen sorption isotherms (A) and PSD (B) of MA-xP-20K

1 Figure 1

Figure 1 Nitrogen sorption isotherms (A) and PSD (B) of typical MA-xP samples. Note that the remaining curves for MA-0.25P, MA-0.75P, MA-1.5P, MA-2P are represented in Supporting Information Figure S1.

1 Figure 2

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4 Figure 2 Small angle x-ray scattering (SAXS) from 0.5° to 5° of typical MA-xP samples

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Figure 3 SEM images of the as-made aluminas: MA (A), MA-1P (B), MA-4P (C) and MA-1P-20K (D). The scale bars are 100 nm. E ~ H are the TEM images of MA-0.25P, MA-0.75P, MA-1P and MA-1P-20K, respectively.

1 Figure 4

4 Figure 4 Nitrogen sorption isotherms (A) and PSD (B) of typical MA-1P-mK samples

1 Figure 5

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4 Figure 5 Wide angle x-ray scattering (WAXS) from 10° to 80° of typical MA-1P-mK
5 samples

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1 Figure 6

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4 Figure 6 Nitrogen sorption isotherms (A) and PSD (B) of MA-xP-20K

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6 Table 4 Adsorption parameters of MA-xP-20K and the catalytic activity in biodiesel
7 synthesis within 2 h reaction

8 Table 5 Methyl ester compositions ~~in the obtained biodiesel~~ in percentage (%) in the
9 biodiesel obtained

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Table 1 Fatty acid compositions of canola oil used herein

Fatty Acid	Composition (wt.%)
C 14:0 Myristic acid	0.04
C 16:0 Palmitic acid	4.00
C 16:1 Palmitoleic acid	0.21
C 18:0 Stearic acid	1.82
C 18:1 Oleic acid	62.89
C 18:2 Linoleic acid	19.62
C 18:3 Linolenic acid	8.47
C 20:0 Arachidic acid	0.62
C 20:1 Eicosenoic acid	1.29
Others	1.04

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Table 2 Adsorption parameters of MA-xP

Samples	BET Surface	Pore Volume	D_a^c	D_p^d
	Area ^a (m ² /g)	V_p^b (cm ³ /g)	(nm)	(nm)
MA	146.6	0.164	3.6	3.5
MA-0.25P	175.5	0.275	5.0	5.7
MA-0.5P	199.9	0.519	7.0	9.0
MA-0.75P	220.8	0.675	8.8	10.7
MA-1P	236.7	0.812	10.1	12.3
MA-1.5P	237.8	1.219	14.9	16.4
MA-2P	241.4	1.446	17.0	19.5
MA-3P	259.8	1.924	20.6	23.0
MA-4P	261.6	2.152	24.3	29.9

2 Note: ^a BET surface area measured in the relative pressure range of 0.05–0.3. ^b The BJH desorption3 cumulative volume of pores between 17.000 Å and 3000.000 Å width. ^c Average pore diameter by BET. ^d4 The peak positions of the distribution curves by BJH. The same abbreviations [we are used in Table 3 and](#)5 [Table 4.](#)

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Table 3 Adsorption parameters of MA-1P-mK and the catalytic activity in biodiesel synthesis within 5 h reaction

Samples	BET Surface	Pore Volume	Da	Dp	Yield of
	Area (m ² /g)	Vp (cm ³ /g)	(nm)	(nm)	Biodiesel
MA-1P	236.7	0.812	10.1	12.3	-
MA-1P-5K	230.2	0.891	11.0	13.7	4.8%
MA-1P-10K	212.4	0.905	12.7	15.0	44.3%
MA-1P-15K	151.2	0.783	16.1	17.5	72.4%
MA-1P-20K	105.7	0.709	19.7	17.3	92.2%
MA-1P-25K	87.1	0.597	20.4	24.5	94.4%

Table 4 Adsorption parameters of MA-xP-20K and the catalytic activity in biodiesel synthesis within 2 h reaction

Samples	BET Surface Area (m ² /g)	Pore Volume Vp (cm ³ /g)	Da (nm)	Dp (nm)	Yield of biodiesel
MA	146.6	0.164	3.6	3.5	-
MA-20K	16.7	0.034	4.0	3.7	29.1%
MA-0.25P	175.5	0.275	5.0	5.7	—
MA-0.25P-20K	68.8	0.201	9.9	12.1	78.9%
MA-0.5P	199.9	0.519	7.0	9.0	-
MA-0.5P-20K	85.8	0.401	14.0	15.0	85.4%
MA-1P	236.7	0.812	10.1	12.3	-
MA-1P-20K	105.7	0.709	16.2	17.3	86.8%

Table 5 Methyl ester compositions ~~in the obtained biodiesel~~ in percentage (%) in the biodiesel obtained

Samples	Yield	Methyl Ester Compositions in the Obtained Biodiesel <u>Obtained</u>				
		(%)				
		C16:0	C18:1	C18:2	C18:3	Others ^a
MA-1P-5K	4.8%	0	77.82	22.18	0	0
MA-1P-10K	44.3%	3.86	64.90	21.48	9.76	0
MA-1P-15K	72.4%	4.27	64.28	20.22	9.43	1.8
MA-1P-20K	92.2%	4.19	63.82	19.88	9.32	2.79
MA-1P-25K	94.4%	4.18	63.88	19.84	9.32	2.78
MA-20K	29.1%	4.26	63.56	20.76	9.20	2.22
MA-0.25P-20K	78.9%	4.11	64.79	20.01	9.24	1.85
MA-0.5P-20K	85.4%	3.99	63.68	20.07	9.25	3.01
MA-1P-20K	86.8%	4.09	63.73	19.93	9.31	2.94

Note: ^a The term “Others” ~~mean~~refers to the remaining methyl esters in the canola oil derived biodiesel, including C14:0, C16:1, C18:0, C20:0, C20:1 and C22:0.