

Ionic Liquid Assisted Fabrication of Mesoporous γ -Al₂O₃

Zhe Tang

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis CNPC
China University of Petroleum
Qingdao, Shandong, China, 266555
tangzhe1983@163.com

Xiaofu Hu

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis CNPC
China University of Petroleum
Qingdao, Shandong, China, 266555

Yunqi Liu

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis CNPC
China University of Petroleum
Qingdao, Shandong, China, 266555

Chenguang Liu

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis CNPC
China University of Petroleum
Qingdao, Shandong, China, 266555

Abstract— Mesoporous γ -Al₂O₃ has been successfully synthesized via an ionic liquid-assisted solvent evaporation process. The results show that ionic liquid [Omim]⁺Cl⁻ plays an important role in the formation of the mesostructure due to its strong interactions with reaction particles. The synthesized porous γ -Al₂O₃ has a larger specific surface area of ca. 356 m²/g with wormlike pore structure. The products are characterized by N₂ porosimetry, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Transmission Electron Microscopy (TEM).

Keywords— alumina; ionic liquid; mesostructure; evaporation.

I. INTRODUCTION

γ -Al₂O₃ is important industrial materials which are used widely as catalyst supports, catalyst, absorbents, ceramics, abrasives and filters^[1,2] due to their unique characteristics. The property and utility of γ -Al₂O₃ can be traced to a favorable combination of textural properties, such as specific area, pore size and pore volume^[3]. Conventional forms of γ -Al₂O₃ typically exhibit a specific area below 250 m²/g and a pore volume less than 0.5 cm³/g^[4]. Hence it is necessary to develop a new route to synthesize γ -Al₂O₃ with a high specific area and pore volume.

Room-temperature ionic liquids (RTILs), a kind of green reagents, have been widely used as media and catalyst^[5], owing to their unique properties^[6]. More recently, RTILs have received considerable attention in synthesis of the novel inorganic materials^[7]. Tongil Kim^[8] has synthesized different γ -Al₂O₃ nanomaterials via an assisted by [bmim]⁺Cl⁻. Although great efforts have been done, there was few reports about the synthesis γ -Al₂O₃ with a high specific area via an ionic liquid-assisted method.

In this paper, we report a facile and environment friendly route to synthesize the mesoporous γ -Al₂O₃ with wormlike pore structure by a one-step ionic liquid-assisted solvent evaporation method. The ionic liquid [Omim]⁺Cl⁻ plays a key role in the formation of the mesostructure.

II. EXPERIMENTAL

A. Preparation

All chemicals are analytical-grade reagents, purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Ionic liquid 1-n-octyl-3-methylimidazolium chloride ([Omim]⁺Cl⁻) was purchased from Shanghai Cheng Jie Chemical Co. Ltd.

The synthesis of the mesoporous γ -Al₂O₃ was similar to the literature^[9]. In a typical synthesis, 2 mmol Al(NO₃)₃·9H₂O and 1 mL citric acid were first dissolved in 20 mL ethanol and 10 mL H₂O at room temperature, 48 mmol [Omim]⁺Cl⁻ was then added into the above solution with vigorous stirring at 60 °C for 24h in water bath, afterwards put it into a drying oven at 60 °C to undergo solvent evaporation process. After 4 days of aging, a colorless and transparent solid was produced. Subsequent calcination at 550 °C for 6 h finally resulted in the formation of porous γ -Al₂O₃ at a heating rate of 2 °C/min

B. Characterization

The crystal structure and phase purity of the products were identified by means of Panalytical X-ray diffraction (XRD, X'Pert PRO MPD) analysis with Cu-K α radiation (λ =1.5406 Å). The sample morphology was checked by scanning electron microscopy (SEM, S-4800, JEOL) and transmission electron microscopy (TEM, JEM-2100UHR, JEOL). The structure characteristics of the samples were further measured by Fourier transform infrared spectra (FT-IR, NEXUS FTIR, NIOLET).

Financial support from the National Basic Research Program of China (No.2010CB226905) and the National Natural Science Foundation, China (No.21176258, U1162203) and Specialized Research Fund for the Doctoral Program of Higher Education, (No.20110133110002) and the Fundamental Research Funds for the Central Universities, (No.27R1104 065A) are gratefully acknowledged.

III. RESULTS AND DISCUSSION

A. Structure characterization

The phase and purity of the products were examined by powder XRD measurement. Figure 1 shows the XRD patterns of the products with or without $[\text{Omim}]^+\text{Cl}^-$. It is evident that all of the expected peaks can be indexed to the cubic $\gamma\text{-Al}_2\text{O}_3$, which are in good agreement with the reported data (JCPDS Card 10-425). Further evidence for the formation of $\gamma\text{-Al}_2\text{O}_3$ can be obtained from their FT-IR spectra (Figure 2). Figure 2 shows the FT-IR spectrum of the products with or without $[\text{Omim}]^+\text{Cl}^-$. All the absorption bands are in good agreement with $\gamma\text{-Al}_2\text{O}_3$ FT-IR data reported in the literature [8]. The intense band at 3465 cm^{-1} and the weak band at 1640 cm^{-1} are attributed to the stretching vibrations of OH groups in the hydroxide structure as well as physically adsorbed water. The intensive bands at 798 and 578 cm^{-1} represent the vibration mode of AlO_6 octahedral. Furthermore, it can be inferred from XRD that the average crystallite sizes of the $\gamma\text{-Al}_2\text{O}_3$ samples with or without $[\text{Omim}]^+\text{Cl}^-$ are about 3.8 and 12.3 nm respectively, according to the Scherrer equation.

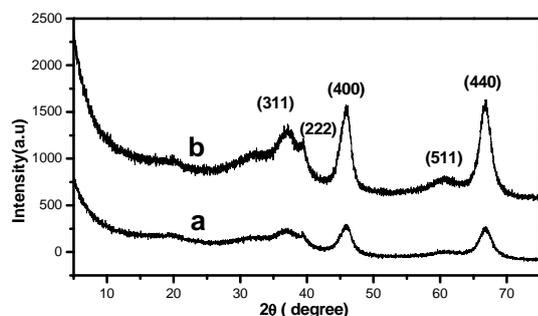


Figure 1. XRD patterns of the products with $[\text{Omim}]^+\text{Cl}^-$ (a) and (b) without $[\text{Omim}]^+\text{Cl}^-$

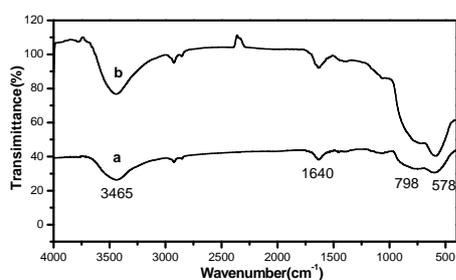


Figure 2. FT-IR spectra of the products with $[\text{Omim}]^+\text{Cl}^-$ (a) and (b) without $[\text{Omim}]^+\text{Cl}^-$

B. Morphology characterization

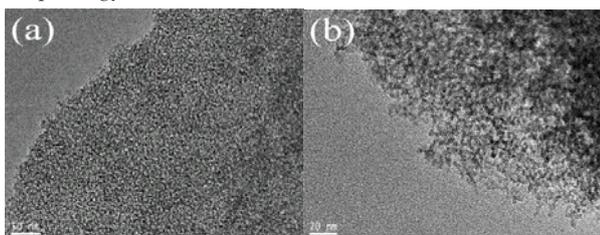


Figure 3. TEM images of the $\gamma\text{-Al}_2\text{O}_3$ samples (a) low- and (b) high-magnification TEM images with $[\text{Omim}]^+\text{Cl}^-$, (c) low- and (d) high-magnification TEM images without $[\text{Omim}]^+\text{Cl}^-$

The TEM images of the $\gamma\text{-Al}_2\text{O}_3$ samples with or without $[\text{Omim}]^+\text{Cl}^-$ are shown in Figure 3. It is evident that ionic liquid $[\text{Omim}]^+\text{Cl}^-$ plays a key role in formation of the mesostructured $\gamma\text{-Al}_2\text{O}_3$ materials. Figures 3a and 3b are the low- and high-magnification TEM images of the $\gamma\text{-Al}_2\text{O}_3$ sample with $[\text{Omim}]^+\text{Cl}^-$. The images show that the $\gamma\text{-Al}_2\text{O}_3$ product owns regularly bicontinuous wormlike mesopore of ca. 3.8 nm in length and ca. 2.0 nm in width and has an aluminum wall of ca. 4.3 nm , which are in good agreement with the result of its XRD. Figures 3c and 3d are the low- and high-magnification TEM images of the $\gamma\text{-Al}_2\text{O}_3$ sample without $[\text{Omim}]^+\text{Cl}^-$. The micrographs show the $\gamma\text{-Al}_2\text{O}_3$ sample is composed of larger nanosheets with ca. 178 nm in width and 200 nm in length, and doesn't form wormlike mesopore, indicating that the $[\text{Omim}]^+\text{Cl}^-$ has an important role in formation of the mesostructured $\gamma\text{-Al}_2\text{O}_3$. The reason may be due to the strong interactions between the ionic liquid and reaction particles, such as electrostatic force, hydrogen bond and $\pi\text{-}\pi$ interaction, which would induce reaction particles forming an ordered structure [10].

C. Textural property characterization

The mesostructured $\gamma\text{-Al}_2\text{O}_3$ is further investigated by N_2 porosimetry (Figure 4). Figure 4a are the N_2 adsorption and desorption isotherms and pore size distribution (inset) for the $\gamma\text{-Al}_2\text{O}_3$ samples with $[\text{Omim}]^+\text{Cl}^-$. It is evident that the N_2 adsorption and desorption isotherms of $\gamma\text{-Al}_2\text{O}_3$ under $[\text{Omim}]^+\text{Cl}^-$ are characteristic of a type IV isotherm with a main type H_1 hysteresis loop and the result of its BJH pore size distribution (the inset images) shows the material has a uniform porous size distribution centered at 3.8 nm , which is consistent with the result of TEM and confirms formation of the mesoporous wormlike structure in the case of $[\text{Omim}]^+\text{Cl}^-$. As a consequence, its BET surface area is up to $355.74\text{ m}^2/\text{g}$ and its pore volume is also $0.45\text{ m}^3/\text{g}$ (Table 1). However, the N_2 adsorption and desorption isotherms of $\gamma\text{-Al}_2\text{O}_3$ without $[\text{Omim}]^+\text{Cl}^-$ (Figure 4b) are characteristic of a type IV isotherm with a type H_3 hysteresis loop, indicating that formation of slit-shaped mesopores. And its BJH pore size distribution shows it possesses quite smaller pores than that of $\gamma\text{-Al}_2\text{O}_3$ under $[\text{Omim}]^+\text{Cl}^-$. Together with its TEM results, it reaches a conclusion that those mesopores in the material without $[\text{Omim}]^+\text{Cl}^-$ presumably arise from the spaces among the nanosheets. Due to formation of the larger nanosheets without $[\text{Omim}]^+\text{Cl}^-$, the BET surface of $\gamma\text{-Al}_2\text{O}_3$ without $[\text{Omim}]^+\text{Cl}^-$ is only $190.83\text{ m}^2/\text{g}$ (Table 1), which is much smaller than that of $\gamma\text{-Al}_2\text{O}_3$ under $[\text{Omim}]^+\text{Cl}^-$. It can be concluded that the

method (ionic liquid assisted solvent evaporation process) is a possible route to synthesize γ -Al₂O₃ with high surface area and uniform mesopore size.

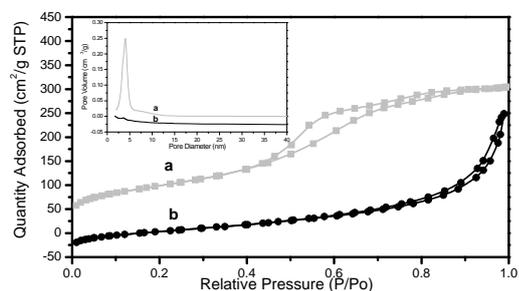


Figure 4. N₂ adsorption and desorption isotherms and pore size distribution (inset) for the γ -Al₂O₃ samples with [Omim]⁺Cl⁻ (a) and (b) without [Omim]⁺Cl⁻

TABLE 1. TEXTURAL PROPERTY OF γ -Al₂O₃ WITH OR WITHOUT [Omim]⁺Cl⁻

Samples	Textural Property			
	BET Surface Area (m ² /g)	T-polt micropore area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Size (nm)
With [Omim] ⁺ Cl ⁻	355.74	-0.0029	0.45	5.27
Without [Omim] ⁺ Cl ⁻	190.83	19.84	0.46	8.27

IV. CONCLUSION

Here, we reported a new method (ionic liquid assisted solvent evaporation process) to synthesize γ -Al₂O₃ with high surface area and uniform mesopore size. The study shows that [Omim]⁺Cl⁻ plays an important role in the formation of mesostructured γ -Al₂O₃ materials with wormlike pore structure, which might be attributed to the strong interactions between the

ionic liquid [Omim]⁺Cl⁻ and reaction particles. However, the detailed mechanism is not clear and still under way nowadays. Furthermore, the method can be applied into synthesizing other inorganic materials with high surface area and uniform mesopore size, and the mesostructured γ -Al₂O₃ developed in the present work have potential applications in catalysts, optical nanodevices.

REFERENCES

- [1] Y. Xia, P. D. Tang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. L. Kim, H. Q. Yan, "One-dimensional nanostructures: synthesis, characterization and application," *Advanced Materials*, vol. 15, pp. 353 - 389, 2003
- [2] J. J. Zhang, Q. Ji, P. Zhang, Y. Z. Xia, Q. S. Kong, "Thermal stability and flame-retardancy mechanism of poly(ethylene terephthalate)/boehmite nanocomposites, *Polymer Degradation and Stability*," vol. 95, pp. 1211 - 1218, 2010
- [3] L. L. Li, W. T. Duan, Q. Yuan, Z. X. Li, H. H. Duan, C. H. Yan, "Hierarchical γ -Al₂O₃ monoliths with highly ordered 2D hexagonal mesopores in macro-porous walls", *Chem. Commun.*, pp. 6174-6176, 2009
- [4] Z. R. Zhang, R. W. Hicks, T. R. Pauly, T. J. Pinnavaia, "Mesostructured Forms of γ -Al₂O₃", *J. Am. Chem. Soc.*, Vol. 124, PP. 1592-1593, 2002
- [5] R. Sheldon, "Catalytic Reactions in Ionic Liquids," *Chem. Commun.*, vol. 23, pp. 2399 - 2407, 2001
- [6] M. J. Earle, K. R. Seddon, "Ionic liquids. Green solvents for the future," *Pure Appl. Chem.*, vol. 72, pp. 1391 - 1398, 2000
- [7] M. Martinis, P. Berton, R. P. Monasterio, R. G. Wuilloud, "Emerging ionic liquid-based techniques for total-metal and metal-speciation analysis," *Trends in Analytical Chemistry*, vol. 29, pp. 1184 - 1201, 2010
- [8] T. Kim, J. B. Lian, J. M. Ma, X. C. Duan, W. J. Zheng, "Morphology Controllable Synthesis of γ -Alumina Nanostructures via an Ionic Liquid-Assisted Hydrothermal Route," *Cryst. Growth Des.* Vol. 10, pp. 2928 - 2933, 2010
- [9] M. Z. Liu, H. M. Yang, "Facile synthesis and characterization of macro-mesoporous γ -Al₂O₃", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 371, PP. 126-130, 2010
- [10] Z. Tang, Y. Q. Liu, G. C. Li, X. F. Hu, C. G. Liu, "Ionic liquid assisted hydrothermal fabrication of hierarchically organized γ -AlOOH hollow sphere", *Materials Research Bulletin*, vol. 47, pp. 3177 - 3184, 2012