Full Paper ____ *Thematic Section:* Research into New Technologies.
The Reference Object Identifier – ROI: jbc-01/20-63-7-126 *Subsection:* Technology of the Inorganic Substances.
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/20-63-7-126
Submitted on July 13, 2020.

Effect of acidity on the properties of silica-aluminas synthesized by sol-gel method

© **Lyubov V. Furda**,* **Evgenia A. Tarasenko**, **Sofya N. Dudina**, and **Olga E. Lebedeva**+
General Chemistry Division. Institute of Pharmacy, Chemistry and Biology.
Belgorod State National Research University. Pobedy St., 85. Belgorod, 308015. Russia.
Phone: +7 (4722) 30-11-66. E-mail: OLebedeva@bsu.edu.ru

*Supervising author; +Corresponding author

Keywords: amorphous silica-aluminas, sol-gel synthesis, porosity, specific surface area, acid-base properties.

Abstract

In the present work amorphous silica-aluminas were synthesized by the coprecipitation method during the hydrolysis of an alcohol solution of tetraethoxysilane (with a tetraethoxysilane: alcohol mass ratio of 1: 1) and 6% aqueous solution of aluminum nitrate at pH values of 1, 3, and 10. The Si/Al molar ratio for all synthesized samples were 4.72 (± 0.29). The amorphous character of the investigated materials was confirmed by X-ray phase analysis. According to the results of scanning electron microscopy, it was found that the resulting powders have particles with a size of 1-20 μm. It was shown that the conditions of synthesis affected the specific surface area and porosity of the materials under study. By the method of low-temperature adsorption-thermodesorption of nitrogen it was established that silica-aluminas obtained under acidic conditions were microporous materials. For the sample obtained under alkaline conditions (pH = 10), the contribution of macropores is very significant. A decrease in surface area is observed as the pH of the synthesis increases. The Hammett indicator method was used to identify and quantify surface centers of different acidity. All studied silica-aluminas are characterized by the presence of both Brønsted basic (pK_a^x from 7 to 12.8) and acidic (pK_a^x from 0 to 7) centers, and Lewis basic (pK_a^x from -4.4 to 0) with a pronounced maximum at pK_a^x = 1.02. It was found that the synthesis conditions had a significant effect on the concentration of active centers. The values of the Hammett function are practically the same for the 3 studied silica-aluminas and describe the studied samples as materials of medium acidity. The variety of Lewis and Brønsted centers on the surface indicates the amphoteric properties of the materials under study. This gives the samples the properties of polyfunctional sorbents and catalysts.

References

[1] O.V. Krylov. Heterogeneous catalysis. *Moscow: IKC «Akademkniga»*. **2004**. 679p. (russian)
[2] S. Peta, T. Zhang, V. Dubovoy, K. Koh, M. Hu, X. Wang, T. Asefa. Template-free synthesis of highly selective amorphous aluminosilicate catalyst for toluene alkylation. *Appl. Catal., A: Gen.* **2018**. Vol.556. P.155-159. DOI:10.1016/j.apcata.2018.02.029.
[3] C. Perego, A. de Angelis, A. Carati, C. Flego, R. Millini, C. Rizzo, G. Bellussi. Amorphous aluminosilicate catalysts for hydroxyalkylation of aniline and phenol. *Appl. Catal., A: Gen.* **2006**. Vol.30. No.12. P.128-136. DOI:10.1016/j.apcata.2006.03.013.
[4] Казаков М.О., Надеина К.А., Климов О.В., Дик П.П., Корякина Г.И., Перейма В.Ю., Сорокина Т.П., Доронин В.П., Князева Е.Е., Иванова И.И., Носков А.С., Головачев В.А., Кондрашев Д.О., Клейменов А.В., Ведерников О.С., Храпов Д.В., Панов А.В. Разработка новых отечественных катализаторов глубокой гидропереработки вакуумного газойля. *Катализ в промышленности*. **2016**. Т.16. №6. С.85-93. DOI:10.18412/1816-0387-2016-6-85-93.
M.O. Kazakov, K.A. Nadeina, O.V. Klimov, P.P. Dick, G.I. Koryakina, V.Yu. Pereima, T.P. Sorokina, V.P. Doronin, E.E. Knyazeva, I.I. Ivanova, A.S. Noskov, V.A. Golovachev, D.O. Kondrashev, A.V. Kleimenov, O.S. Vedernikov, D.V. Khrapov, A.V. Panov. Development of new domestic catalysts for deep hydroprocessing of vacuum gasoil. *Catalysis in industry.* **2016**. Vol.16. No.6. P.85-93. DOI:10.18412/1816-0387-2016-6-85-93
[5] T.C. Keller, J. Arras, M.O. Haus, R. Hauert, A. Kenvin, J. Kenvin, J. Pérez-Ramírez. Synthesis-property-performance relationships of amorphous silica-alumina catalysts for the production of methylenedianiline and higher homologues. *J. Catal.* **2016**. Vol.344. P.757-767. DOI: 10.1016/j.jcat.2016.08.016

[6] N. Yao, G. Xiong, M. He, S. Sheng, W. Yang, X. Bao. A novel method to synthesize amorphous silica–alumina materials with mesoporous distribution without using templates and pore-regulating agents. *Chem. Mater.* **2002**. Vol.14. No.1. P.122-129. DOI: 10.1021/cm010270w
[7] Y.Y. Ge, Z.Q. Jia, H.T. Li, P. Gao, Y. Zhang. Amorphous aluminosilicates used as acid catalysts for tetrahydrofuran polymerizatio. *Reac. Kinet. Mech. Cat.* **2014**. Vol.112. P.467-475. DOI:10.1007/s11144-014-0714-2
[8] V.Y. Pereyma, P.P. Dik, O.V. Klimov, S.V. Budukva, K.A. Leonova, A.S. Noskov. Hydrocracking of vacuum gas oil in the presence of catalysts NiMo/Al_2O_3–amorphous aluminosilicates and NiW/Al_2O_3–amorphous aluminosilicates. *Russ. J. Appl. Chem.* **2015**. Vol.88. No.12. P.1969-1975. DOI:10.1134/S10704272150120113
[9] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani, R.J. Willey. FT-IR studies on light olefin skeletal isomerization catalysis: III. Surface acidity and activity of amorphous and crystalline catalysts belonging to the SiO_2–Al_2O_3 system. *J. Catal*. **1998**. Vol.179. No.2. P.581-596. DOI: 10.1006/jcat.1998.2251.
[10] D. Rio, A. Aguilera-Alvarado, I. Cano-Aguilera, M. Martinez-Rosales and S. Holmes. Synthesis and characterization of mesoporous aluminosilicates for copper removal from aqueous medium. *Materials Sciences and Applications*. **2012**. Vol.3. No.7. P.485-491. DOI:10.4236/msa.2012.37068.
[11] A.S. Shilina, V.K. Milinchuk. Sorption purification of natural and industrial waters from cations of heavy metals and radionuclides by a new type of high-temperature aluminosilicate adsorbent. *Sorption and chromatographic processes*. **2010**. Vol.10. Iss.2. P.237-245. (russian)
[12] E.J.M. Hensen, D.G. Poduval, P.C.M.M. Magusin, A.E. Coumans, Veen, van, J.A.R. Formation of acid sites in amorphous silica-alumina. *J. Catal*. **2010**. Vol.269. No.1. P.201-218. DOI:10.1016/j.jcat.2009.11.008
[13] A. Chaumonnot, F. Tihay, A. Coupe, S. Pega, C. Boissiere, D. Grosso, C. Sanchez. New aluminosilicate materials with hierarchical porosity generated by aerosol process. *Oil Gas Sci. and Technol.* **2009**. Vol.64. No.6. P.681-696. DOI: 10.2516/ogst/2009029
[14] L.V. Furda, D.E. Smalchenko, E.N. Titov, O.E. Lebedeva. Thermocatalytic destruction of polypropylene in the presence of aluminosilicates. *Proceedings of universities. Chemistry and chemical technology.* **2020**. Vol.63. Iss.6. P.85-89. DOI: 10.6060/ivkkt.20206306.6202
[15] K. Tanabe. Solid acids and base. Their catalytic properties. *Academic press, New York-London.* **1970**. 183p.
[16] S.J. Gregg, K.S.W. Sing, K.S. Sing. Adsorption, Surface Area, and Porosity. *Academic press.* **1991**. 303p.