

Synthesis and characterization of a novel mesoporous Al-KMSU silica catalyst with high thermal stability

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ABSTRACT

A novel Aluminium incorporated mesoporous catalyst was synthesized from silica source and hydrocarbon template. We have carried out several characterizations for investigating the physical and chemical properties of mesoporous Al-KMSU catalyst. X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) and Thermo gravimetric analysis (TGA) measurements revealed that the synthesized catalyst have large porosity and high thermal stability. The material surface morphology was confirmed by Scanning Electron Micrograph (SEM). Temperature-programmed desorption (TPD) analysis confirmed the existence of acid sites on its surface.

KEY WORDS: mesoporous material, template, thermal stability, large pore, acid sites.

1. INTRODUCTION

Solid acid catalysis plays an important role in modern chemical industry because of their unique properties. The properties like homogeneity of the pores, high surface area, and good thermal stability, make them an attractive molecular sieve for applications in catalysis, sorption etc. To develop a solid acid catalyst various techniques were applied by several researchers. Here we have adopted simple technique to synthesize Al-KMSU catalyst. Because of the potential applications of Al-KMSU materials as catalysts, it is very necessary to investigate and understand the incorporation of metal atoms and their catalytic property.

2. EXPERIMENTAL

The Al-KMSU is prepared by using the hydrocarbon of alkyl (chain length C_{12}) as a template. The molar composition of the resultant mixture is $0.08 Na_2SiO_3 : X Al_2(SO_4)_3 : 8 H_2O : 0.02 C_{12}H_{26}$ (X-varies with the Si/Al ratio). Sodium silicate (23 g) and Aluminium sulphate are dissolved in water (140 ml) under stirring. Then template is added into the solution. The resultant mixture is stirred for 2 h at room temperature and the pH of the mixture is adjusted to 10 by the drop wise addition of concentrated sulphuric acid. The gel is aged at room temperature for 48 h and heated on hot plate to evaporate water and to attain complete crystallization of the molecular sieves. The sample is washed by using distilled water and dried at $110^\circ C$ in hot air oven for 2 h. The sample is calcinated in the presence of air until all the impurities and template are completely removed from the pores of molecular sieves.

3. RESULTS AND DISCUSSION

The diffraction patterns show admirable quality with typical low angle characteristic very strong peak at lower 2θ value 0.7 deg and weaker peaks at higher 2θ value at 1.1 and 1.2 deg. They correspond to the planes 100, 110 and 200, respectively. Fig.1(a) indicates that incorporation of aluminum results in a shift of the main strong peak to lower 2θ values. This is consistent with the presence of tetrahedral aluminum in the KMSU framework and is due to the longer Al-O bond length compared to the Si-O bond. The peaks existed in the lower 2θ value indicates the lacking of long range order in the crystalline Al-KMSU catalyst.

The N_2 adsorption/desorption isotherms and pore size distribution curves of the calcined mesoporous Al-KMSU material are shown in Fig.1(b). The isotherms can be classified as type IV isotherms according to IUPAC nomenclature. A linear increase of absorbed volume is obvious at low relative pressure ($p/p_0 < 0.1$) for each sample, which can be ascribed to the mono-layer adsorption. With the increasing of relative pressure, multi-layer adsorption starts and the isotherm exhibited that the adsorption amount increased abruptly at relative pressure (P/P_0) 0.40–0.50 due to the capillary condensation in mesopores. The isotherm exhibited pronounced steep condensation step for relative pressures 0.6 - 0.9 arising from condensation of nitrogen inside the mesopores and indicating the wide range of mesopore formation within the tetrahedral framework of the Al-KMSU molecular sieves.

Thermo gravimetric analysis of the catalyst fig.1(c) shows distinct weight losses that depend on framework composition. Three different regions of weight loss are noted in the temperature range $50-150^\circ C$, $150-268^\circ C$ and $268-523.3^\circ C$. The first weight loss (16.2 %) corresponds to desorption and removal of the water molecules physisorbed on the external surface of the crystallites and low amount of organic template. The second, weight loss (15.8 %) between $150-268.4^\circ C$ is related to water loss from the condensation of adjacent silanol groups to form siloxane bond and decomposition of residual surfactants. Finally, the last 1.9% weight loss from 268 to $523^\circ C$ is attributed to condensation of residual silanol groups. The additional increase of temperature reveals that there is no weight loss in the material. The result clearly reveals that the mesoporous Al-KMSU materials produced in the

present work had good thermal stability. However, the regular weight loss depends on the framework or substituted silicon to metal ratio. Thus, weight loss was higher in the low metal contents.

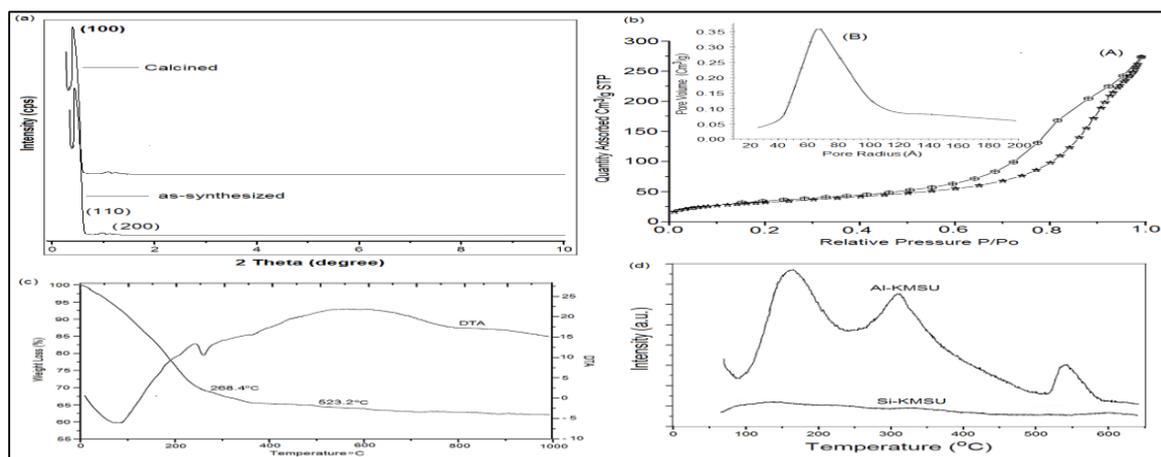


Figure.1.Characterization results for the Al-KMSU molecular sieve

The temperature-programmed desorption of ammonia (NH_3 -TPD) was performed to determine the amount and the strength of acid sites on the catalysts and the results are displayed in Fig.1(d) Al-KMSU silica catalyst TPD spectra of NH_3 showed a low-temperature peak at 150°C to 160°C . This is due to the weakly adsorbed NH_3 in Lewis acid sites. The medium and a high temperature peak appeared at 325°C and 500°C to 550°C are attributed to the presence of Bronsted acid sites in the molecular sieves.

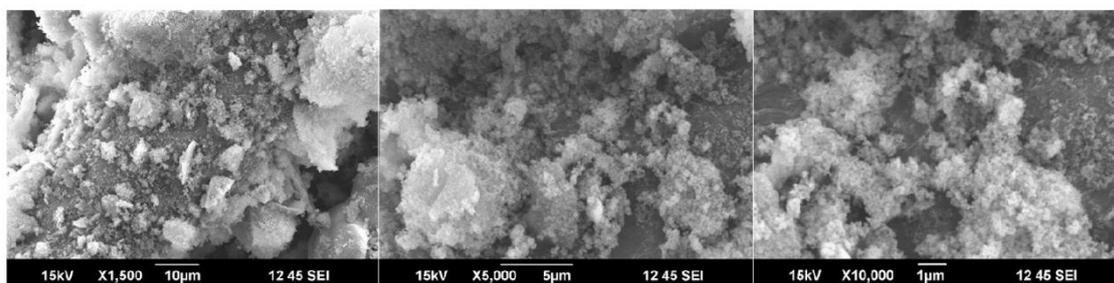


Figure.2.SEM micrograph of mesoporous Al-KMSU molecular sieve

The morphology, size and size distribution of the Al-KMSU particles are determined by scanning electron microscopy. The calcined sample particles have a distorted spherical shape. The particle size is ranged from 200 to 250 nanometers.

4. CONCLUSION

It is concluded that the characterization technique confirms the formation of novel Al incorporated mesoporous hexagonal silica based molecular sieves with large pore and high thermal stability by using hydrocarbon as a template. The existence of Bronsted and Lewis acid sites confirms that the catalyst has excellent solid acid activity for chemical reactions.

REFERENCES

- Amit Dubey, Divya Sachdev and Neel Mani Srivasatava, Synthesis, characterization and catalytic application of ordered mesoporous silica nano composites functionalized with chloroacetic acid (SBA-15/CA), *Adv. Mat. Lett.*, 4 (1), 2013, 39-45.
- Anunziata A, Martinez M.L, and Beltramone A.R, Hydroxyapatite/MCM-41 and SBA-15 Nano-Composites: Preparation, Characterization and Applications, *Materials*, 2, 2009, 1508.
- Araujo R.S, Synthesis and characterization of Al- and Ti-MCM-41 materials: application to oxidation of anthracene, *Braz. J. Chem. Eng.*, 24, 2007.
- Hector Ivan Melendez-Ortiz, Hydrothermal Synthesis of Mesoporous Silica MCM-41 Using Commercial Sodium Silicate, *J. Mex. Chem. Soc.*, 57 (2), 2013, 73-79.
- Kannan C, Muthuraja K, and Devi M.R, Hazardous dyes removal from aqueous solution over mesoporous aluminophosphate with textural porosity by adsorption, *J. Hazard. Mater.*, 10, 2013, 244-245.

Kannan C, Sivakami K, and Ilavarasi Jeyamalar J, A simple method for the synthesis of thermally stable large pore mesoporous aluminophosphate molecular sieves, *Mater. Lett.*, 113, 2013, 93.

Lianchi Liu, Lifeng Zhao, and Huai Sun, Simulation of NH₃ Temperature-Programmed Desorption Curves Using an ab Initio Force Field, *J. Phys. Chem. C*, 113, 2009, 16051–16057.

Mohammad Teymouri, Abdolraouf Samadi-Maybodi, Amir Vahid, A Rapid Method for the Synthesis of Highly Ordered MCM-41, *Int. Nano Lett.*, 1, 2011, 34-37.