

Pore-expanded MCM-41 Aluminosilicate for Acid-Catalyzed Reactions: Direct (One-pot) versus Post Aluminations

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Introduction

Selective ring opening (SRO) of polynuclear aromatics has been proposed as an alternative technology to the existing aromatic upgrading technologies (i.e. catalytic aromatic saturation and hydrocracking) [1]. This energy technology was shown to achieve high cetane number upto the current fuel specifications without the loss of reactant molecular weight. However, the extent of achieving such improvements via SRO depends significantly on the nature of catalyst structure, in particular the support. Existing catalyst supports (i.e. zeolites, mixed oxides, and metal doped conventional MCM-41) failed to address the essential aspects needed for the SRO process, i.e. the diffusion and the optimal acidity.

Pore-expanded MCM-41 (PE-MCM-41) was prepared by our group [3] via post-synthesis hydrothermal treatment of as-synthesized MCM-41 in the presence of *N,N*-dimethyldodecylamine as an auxiliary swelling reagent. It exhibits distinctive properties such as high specific surface area (ca. 1000 m²/g), large pore size (up to 25 nm), and pore volume (up to 3.5 cm³/g) [3]. The utilization of PE-MCM-41 as a catalyst support for the SRO process will provide numerous advantages over the existing supports. These advantages include the rapid diffusion of bulky hydrocarbons, and significant reduction in the deactivation rate, thus improving the on-stream and long-term stability. Our recent work showed that it is possible to obtain aluminosilicate MCM-41 with large pore dimensions and high levels of tetrahedral aluminum via direct (one-pot) hydrothermal synthesis. These materials also displayed mild acidity, and enhanced on-stream stability for the skeletal isomerization reaction. Incorporation of Al onto mesoporous MCM-41 via post synthesis has been shown to cause less structural disordering, and enhances the acid density and the stability [4,5]. Therefore, a study has been undertaken in order to evaluate the preparation via post synthesis and compare it to the direct hydrothermal synthesis in order to determine the effective method that will allow the preparation of large and stable pore-expanded aluminosilicate MCM-41 (PE-Al-MCM-41).

Materials and Methods

PE-Al-MCM-41 with varying contents of aluminum (Si/Al = 10-100) was synthesized via post Aluminations. Details on the preparation of PE-MCM-41 are given in [3]. Two different methods were used for the post Aluminations, aqueous and non-aqueous methods. The starting material for the post Aluminations in non-aqueous solution using aluminum isopropoxide as a source of Al was the calcined dry PE-MCM-41. The starting material for the aqueous method was the as-synthesized PE-MCM-41 using sodium aluminate and aluminum sulphate. In a typical preparation, the appropriate amount of aluminum source was dissolved in water or dry n-hexane (depending on the method) and let stir at ambient temperature for 3 h. Then, 2.0 g of starting material was added and the resulting mixture was

stirred for 24 h at ambient temperature. The obtained powder was dried at 70°C and then calcined at 550 °C for 5h. Several characterization techniques such as BET surface area, XRD, and ²⁷Al and ²⁹Si MAS NMR were used to examine the textural and structural properties. The hydrothermal stability was performed for the powdered calcined samples. These samples were subjected to steam at different temperatures for different period of time. The samples were then recovered by filtration and dried at 120 °C. The mechanical stability was also evaluated by compressing the calcined samples in a 13 mm die at various pressures for 10 min. For subsequent characterization, the samples were crushed to powders. The skeletal isomerization activity was carried out in a fixed bed continuous-flow stainless-steel tubular reactor using cyclohexene as a model molecule. The reaction temperature was varied in the range of 250-450 °C (with 50 °C intervals), and the weight hourly space velocity in the range of 0.5-2 h⁻¹ (with 0.5 h⁻¹ interval).

Results and Discussion

The preliminary results showed that it is possible to obtain pore-expanded aluminosilicate MCM-41 with large pore diameter (ca. 8.5 nm), and enhanced surface acidity via post aluminations using either aqueous or non-aqueous methods. These results were suggested by the N₂ adsorption-desorption and ²⁷Al MAS NMR. It appears also that the structural and textural properties depend significantly on the amount and source of aluminum, preparation methods, and the pH (presence of tetramethylammonium hydroxide (TMAOH)). This can be attributed to the fact that all these factors are expected to play a significant role in the composition of aluminations solution, which will subsequently affect the amount of Al inserted as a framework tetrahedral. These framework species are the origin of the Brønsted acid sites. The acidic properties examined by temperature-programmed desorption and FT-IR of chemisorbed ammonia will be presented as well. The skeletal isomerization of cyclohexene, which is used as a model reaction for the selective ring opening of PNAs, will be also discussed. All characterizations, stability, and catalytic activity results will be compared to those obtained by direct hydrothermal synthesis method.

Significance

This work is of great significance to both the petroleum refining industry and the environment, since it may help to significantly reduce the amount of polynuclear aromatics in heavy crude. Furthermore, it will provide significant advances in the area of supported catalyst design within the context of important industrial and environmental applications.

References

- [1] G. B. McVicker, M. Daage, M. S. Touvelle, C. W. Hudson, D. P. Klein, W. C. Baird Jr., B. R. Cook, J. G. Chen, S. Hantzer, D. E. W. Vaughan, E. S. Ellis, O. C. Feeley, *J. Catal.* **210** (2002) 137. G. B. McVicker, M. Daage, *J. Catal.* **210** (2002) 137.
- [2] H. Du, C. Fairbridge, H. Yang, Z. Ring, *Appl. Catal. A Gen.* **294** (2005) 1.
- [3] A. Sayari, M. Kruk, M. Jaroniec and I.L. Moudrakovski, *Adv. Mater.* **10** (1998) 1376.
- [4] C. Y. Chen, S. L. Burkett, H-X. Li, M. E. Davis, *Microporous Mater.*, **2** (1993) 27.
- [5] R. Mokaya and W. Jones, *Chem. Commun.*, (1997) 2185.