

Pore-Expanded MCM-41 Aluminosilicate Bifunctional Catalysts for the Selective Ring Opening of Polynuclear Aromatics

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Introduction

The increasingly stringent environmental regulation, around the globe, concerning exhaust emissions implies the use of clean fuels with maximum combustion effectiveness (i.e. diesel and kerosene distillates) in order to avoid the particulate matters emissions. This type of emissions is mainly related to the high concentration of multiring polynuclear aromatics (PNAs) contained in fuels [1]. Therefore, the removal of these aromatic hydrocarbons is of utmost importance to the refining industry nowadays. The current technologies for aromatics upgrading, such as aromatic saturation and hydrocracking are limited and far from being able to satisfy the current and future stringent fuel specifications [2,3]. Selective ring opening (SRO) of polynuclear aromatics has been proposed recently as an alternative technology [2]. This energy technology was shown to achieve high cetane number upto the current fuel specifications without the loss of reactant molecular weight. The extent of achieving such improvements via SRO depends significantly on the nature of catalyst structure, in particular the support [4,5]. Our recent work showed that it is possible to prepare an aluminosilicate MCM-41 with large pore diameter, practical stability, and mild acidity, which are all essential precondition for the SRO of bulky PNAs compounds. In this presentation, we will describe the study that has been and still being carried out in order to evaluate the pore-expanded aluminosilicate as a support for the bifunctional catalysts used in the SRO process of PNAs compounds.

Materials and Methods

Pore-expanded aluminosilicates MCM-41 with Si/Al molar ratio of 10-100 was prepared by direct and post synthesis. Bimetallic (Pt-Pd) as 1.0-3.0 wt.%, with a Pt/Pd weight ratio of 1 were supported on PE-Al-MCM-41 by incipient wetness impregnation using aqueous solutions of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and PdCl_2 . Three different impregnation methods were used, the co-impregnation (Pt-Pd), sequential (Pt→Pd), and reverse sequential impregnation (Pd→Pt). After impregnation, solids were first left at 60 °C for 10 h. for slow evaporation of water, dried overnight at 120°C and finally calcined in air at 550 °C for 5 h. 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, temperature-programmed desorption and FT-IR of chemisorbed ammonia, H_2 -temperature-programmed reduction (H_2 -TPR), TEM, and XPS used to examine the textural, structural and surface properties. The catalytic activity of reduced PtPd/PE-AlMCM-41 in the SRO of decalin was carried out in a fixed bed continuous-flow stainless-steel tubular reactor. The effect of temperature (250-500 °C), WHSV (0.5-2.0 h^{-1}), and hydrogen pressure (0.7-3.7 MPa) on the conversion and product distributions were examined.

Results and Discussion

A brief overview of the main textural and structural properties of PE-Al-MCM-41 will be discussed in order to outline the outstanding properties of this material. The dispersion of impregnated metals, which will be evaluated by the XRD, XPS and CO chemisorption measurements will be presented. Furthermore, the nature of reduced species and the extent of metal-support interactions, which will be obtained by H_2 -TPR will be discussed. The particle sizes, which have been shown to play major role in the catalytic activity of bifunctional catalysts [2], will be presented as well. The effect of support structure and preparation, and incorporation methods and content of Pt-Pd metal on the SRO of decalin will be presented as well. Moreover, we will show the effect of temperature and contact time on the conversion and product distributions of the SRO of decalin. More importantly, the catalytic activities of both fresh (on-stream stability) and regenerated (long-term stability) catalysts for a period of one week will be shown. The carbonaceous deposits (coke) on the surface of spent catalysts, which will be characterized using a variety of techniques such as thermal analysis, carbon-hydrogen analyzer and ^{13}C MAS NMR will be presented and correlated to the evaluated catalytic activity. The physico-chemical properties and the catalytic activities of Pt-Pd loaded onto PE-Al-MCM-41 will be compared to those of bimetallic Pt-Pd loaded onto the traditional Al-MCM-41.

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

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