

Review

Silicoaluminophosphate molecular sieves as potential catalysts for hydroisomerization of alkanes and alkenes



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ABSTRACT

Hydroisomerization of light linear naphtha hydrocarbons yield *iso*-alkanes and alkenes of C₄–C₈, which are capable of raising the octane number in a gasoline pool. Zeolite and zeolite-like molecular sieves such as silicoaluminophosphates (SAPOs) with appropriate chemical and structural modification yielded the desired product. This article presents an overview of the various molecular sieve catalysts, their structural modifications, and the reaction conditions utilized for the hydroisomerization of hydrocarbons. In particular, the emphasis on the role of SAPO based molecular sieves and their importance in the tuning of hydroisomerization products are elaborated in detail herein.

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1. Introduction

Hydroisomerization is one of the most important reactions in industrial processes such as fine chemical and petrochemical industries. Hydroisomerization was developed during World War II to upgrade the octane number of gasoline by producing isobutene [1]. In the petrochemical industry, hydroisomerization reactions are used to upgrade the octane number, which helps in increasing fuel efficiency. Nowadays, the focus has shifted to light straight chain C₅–C₈ paraffins as feeds for hydroisomerization. The branched isomers of C₅–C₈ paraffins possess a higher octane number compared to the corresponding linear paraffins (C₇) outlined in Scheme 1. Thus, hydroisomerization helps to increase the octane number by 10–20, when added to the gasoline pool [2,3].

After the global oil crises of the 1970s and the recognition of climate change in the 1990s owing to the release of greenhouse gases, emphasis was laid on the development of systems, which could serve as alternatives to fossil fuels, as well as improvement of the refining process to decrease the greenhouse gas effect [4]. According to the international charter on clean fuels, the olefin content of gasoline must have a marginal value of 20 vol%. The removal of the olefinic content from gasoline decreases the octane number. Furthermore, it has become important to develop systems/processes, which could increase the octane number of gasoline while reducing its olefin content. Hydroisomerization and aromatization reactions could potentially play an important role in realizing this goal [5].

Initially, the hydroisomerization of *n*-butane was studied using aluminum chloride in systems employing an acidic Friedel–Crafts type catalyst [6] while the dual functional catalysts were developed much later [7,8]. These hydroisomerization processes had several limitations because they required careful handling, catalyst extraction, disposal of waste, and led to reactor and plant corrosion. These problems were solved by the development of solid acid catalyst systems [9]. In the family of solid acid catalysts, amorphous silica–alumina, zeolites, and zeolite-like materials with different pore opening (Fig. 1) have been widely studied for applications in various petrochemical and refinery processes [6]. In particular, zeolite and zeolite-like molecular sieve materials possess high

internal surface area and adsorption capacity, as well as the ability to control the nature (Brønsted and Lewis acidic sites), amount and strength of acidic sites [10–12]. The solid acid catalyst possessing higher surface area exposes more active acidic sites on the surface, which allows reactants to easily access the active sites and favored for hydroisomerization. The hydroisomerization of paraffin proceeds by C–C and C–H activation through carbenium ion formation, which shows direct relation to the amount of acidic sites (Brønsted and Lewis) present on the surface [13]. The presence of strong acidic sites favored the cracking of hydrocarbons [13] and moderate acidic sites are suitable for hydroisomerization. Further, molecular sieve materials possess large pore volume, high adsorption capacity, and ability to reversibly adsorb molecule [14] showed its molecular transfer property. In this regard, it is noteworthy that SAPO-*n* molecular sieve materials, analogous to zeolites, are promising materials for use as catalysts and adsorbents in petrochemical processes such as hydroisomerization, and methanol-to-olefin conversion. In this study, we have focused on the role of SAPO in the hydroisomerization of various *n*-paraffins, and the factors affecting product selectivity and conversion. Considering the importance of SAPO systems in the petrochemical and fine chemical industries, their catalytic activity and reaction conditions (temperature, pressure, metal loading, etc.), and the behavior of different SAPO systems on hydroisomerization reactions are discussed herein.

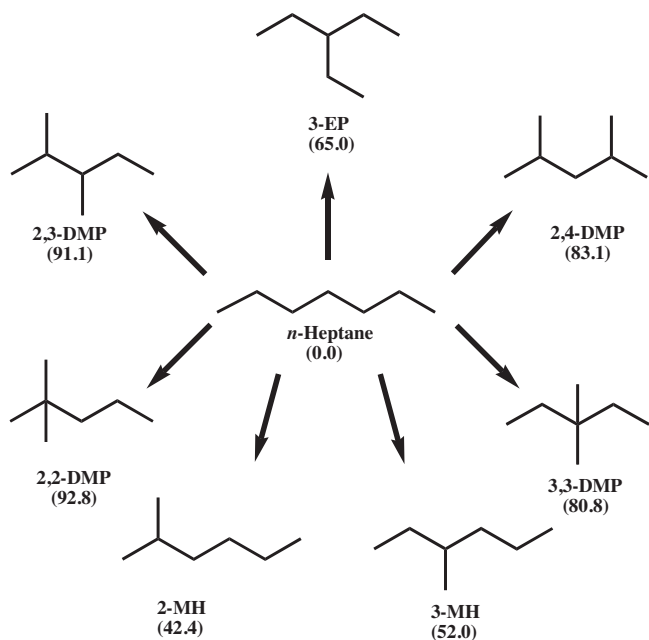
2. Background

2.1. Introduction to zeolite

Molecular sieve materials are class of materials which exhibit the property of acting as sieve on a molecular scale. The most important molecular sieve materials used in hydroisomerization reaction are zeolite and zeolite like silicoaluminophosphate (SAPO) materials [15–18]. Zeolites are framework aluminosilicates which are based on three dimensional network of (SiO₄)⁴⁻ and (AlO₄)⁵⁻ tetrahedra [15]. Zeolites have a wide range of applications in ion exchange [19,20], sorption [21,22], catalysis [23–27], etc. As heterogeneous catalysts, zeolites play an important role in the petrochemical industry, and cracking and synthesis of fine chemicals [9,28]. One of the most important properties of zeolites is shape selectivity. Shape selective reactions occur by mass transfer and involve “configurational diffusion”, i.e., when the diameter of the molecule approaches the structural dimensions of the catalyst, it enters into the cavity [29–32]. Shape selectivity involves: three widely accepted types and are shown in Fig. 2, which involves:

- Reactant shape selectivity, which distinguishes competitive reactants and allows only the appropriate reactants, based on the pore size, to enter into the cavity for the reaction, e.g., selective catalytic “dewaxing” of waxy distillates and lube fractions over ZSM-5.
- Product shape selectivity, which makes it possible for various products to form in the channels of zeolites. However, only those products which are small enough compared to the dimension of the pores exit, e.g., toluene disproportionation to yield para-xylene.
- Transition state selectivity, wherein the pores are such that the effective diameter of the pore inhibits the formation of unstable transition states or intermediates, e.g., alkylation of aromatics [19].

Nevertheless, certain shape selective theories are currently disputable, and these include inverse shape selectivity, molecular traffic control, pore mouth-key-lock shape selectivity, window and nest effects [29,30]. It is important to specify that the recently



Scheme 1. Important isomerization reactions along with corresponding octane number of feed and product.

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