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Applications of Zeolite with Additives in Petroleum Refinery

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Abstract

In the last century, catalysts became one of the most powerful tools in the petroleum refining industry. Zeolite widely used as catalysts and catalyst supports for a quite broad range of processes. Zeolite with additives has found widespread application for fluid catalytic cracking operation. This review will focus on the use of various modified zeolites as catalysts and additive in the petroleum refinery. Zeolites with additives are taken different Si /Al ratio. It will more emphasize on new refinery applications such as nitrogen and sulphur remove from gasoline. Many additives likes MCM-22, MCM-41, ZSM-5, and H-ZSM-5 have been reviewed in this paper.

Keyword: Zeolite; Additives; Nitrogen & Sulphur compounds; ZSM-5.

1. Introduction

ZSM-5 with zeolites is different SiO_2/Al_2O_3 alkali-treated ratios. Zeolites are crystalline silicates and aluminosilicates linked through oxygen atoms, producing a three-dimensional network containing and cavities of molecular dimensions. Crystalline structures of the zeolite type but with coordinated Si, Al, or P as well as transition metals. The changes observed are largely influenced by the SiO_2/Al_2O_3 ratios with which the zeolites are synthesized. The sizes of the ZSM-5 particles have a strong effect on the changes in product yields and gas and gasoline compositions. And the performance of HZSM-5 zeolites of varying acidity and porosity were prepared under various synthesis conditions and the effect of catalyst properties on the conversion of ethanol to gasoline reaction were investigated. Alkali-treated ZSM-5 zeolites produce higher yields of light olefins compared to either untreated zeolites or alkali-treatment introduces mesopores to the zeolites and improves their catalytic cracking ability. Zeolites are crystalline, hydrated aluminosilicates having microporous, regular structures. The zeolite micropores are of molecular size which give them adsorption, catalytic and ion exchange properties of paramount importance in both the chemical industrial field and the study of new applications related to process intensification [1], green chemistry [2], hybrid materials [3], medicine [4], animal food uses [5], optical and electrical based applications [6], reaction [7] and sensing [8] microsystems, and nanotechnology [9]. Furthermore, the concept of zeolite can be extended to the so-called porous-tailored materials. Zeolite catalysts have been the source of major improvements in gasoline yield and octane as well as in the production of cleaner fuels and lubricants with enhanced performance properties. Credible reviews zeolite catalysts in petroleum refining processes are already available in a text by Chen et al. It will also highlight several new areas where zeolites are providing improved petroleum products or where they are helping to reduce cost and production of wasteful by-products. FCC process uses an HZSM-5 catalyst due to its high surface area, acidic nature of its pores and well-defined porous structure [4]. However, the HZSM-5 catalyst suffers from low selectivity towards C_5-C_{10} alkanes, high yields of aromatics and carbon deposition thus requiring frequent regeneration. Catalytic dehydration of ethanol to ethylene, disproportionate of ethanol to propylene and ethanol to aromatics are some of the studies reported in this direction, where the textural properties of ZSM-5 zeolite, especially its framework Si/Al, which is related to the acidity of the catalyst, played a vital role in determining the nature of the product [5-7]. The most previous commercial additives usually pre-deactivated. High-temperature (750-850 °C) steam pretreatment is usually applied to the deactivation of ZSM-5 occurring in the commercial unit Octane enhancement. When ZSM-5 Catalyst is added (either fresh or steam deactivated), the gasoline yield will less and C_3–C_4 unsaturated (olefins) yield will be effected. Since HZSM-5 is a typical acid function zeolitic catalyst, the changes in acidity of ZSM-5 caused by different initial Si/Al ratios, chemical dealumination, or steam deactivation with the observed changes in octane number and product yields.

2. The Structure of Catalyst

The crystalline aluminosilicates are highly thermally and hydrothermally stable materials owing to their crystalline structure formed by Si and Al tetrahedral coordinated with oxygen and connected through oxygen bridges. The stability of these materials increases with increasing Si/Al ratio in the structure, and their structure remains stable at temperatures as high as 900 ^{0}C. The thermal and hydrothermal stability is a property of paramount importance in catalysis, considering that there are processes which occur at temperatures of up to 650 ^{0}C. Furthermore the catalyst, when deactivated by coke deposition, should be regenerated at temperatures up to750 ^{0}C and in the presence of steam. The number and strength of acid sites can be controlled. In the case of zeolites, the isomorphous substitution of a Si by a tetrahedrally coordinated Al generates a negative charge on the framework, which is compensated by the presence of cations and which can be directly or indirectly exchanged by H'. Thus, the number and strength of these acid sites can be modified and modulated by changing the chemical composition.

3. Zeolites as Cracking Catalysts

The zeolite thus prepared retained more crystallinity after hydrothermal treatments than the existing commercial ones, with the corresponding benefit in activity for gasoil cracking from the point of view of the selectivity, and owing to its smaller crystallite size. Figure1,2:The four main characteristics of zeolites are their tetrahedral framework, their cavity system, and the presence of water and charge compensating cations in well defined crystallographic positions. The last two would not be strictly applicable in all cases but depend on the chemical composition (Si/Al ratio) of the zeolite. Besides, from a practical point of view, zeolites are environmental-friendly in technological processes [12].

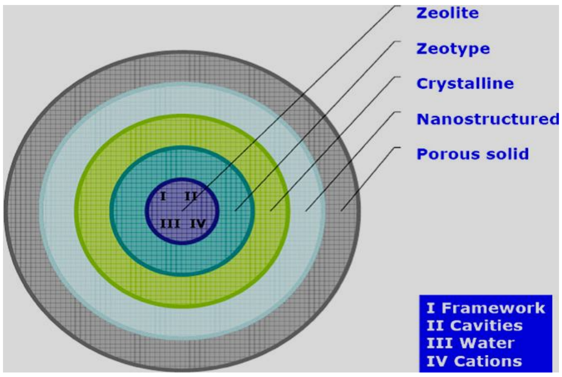

Figure 1: Porous solids and zeolites[4].

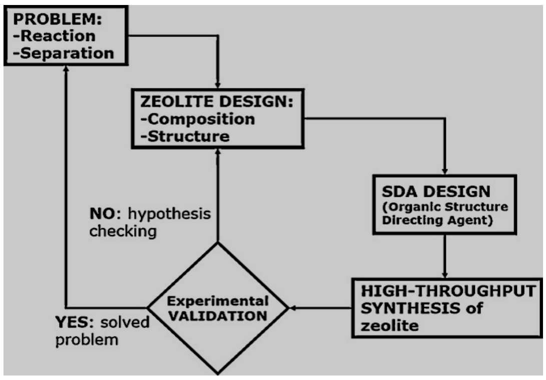

Figure 2: Optimization of zeolite synthesis and application[4].

4. Control Zeolite Crystal Size

The control of the size when synthesizing a zeolite is critical whether the goal is either a catalytic process [21] or an adsorption application [22], but also when the target is the use of zeolites as fillers for mixed matrix membranes [14] or when crystallizing a continuous layer of zeolite [14]. The range of useful particle sizes is wide, from colloidal zeolites, a few tens of nm in size. Colloidal zeolites can be used as seeds for secondary seeded growth and growing larger crystals or membranes, and are also interesting for catalytic and adsorptive applications in view of their high external specific surface areas and reduced diffusion path lengths. Nanozeolites may present inherent problems of pressure drop and safe management due to the possibility of forming respirable aerosols, among others, which have been overcome through the formation of hierarchical pore system materials [15, 16]. Recently, techniques for the growth of large single crystals of various zeolites have been established [15, 19]. Large zeolitic crystals can be of interest for structure refining [18], characterization [21], catalytic [17], electronic [18] and sensing [18] applications, in situ reaction studies [19, 20], and for the study of chemical and physical processes difficult to observe on nanometric or micrometric particles [20].

5. Synthesis of Zeolitized Mesoporous Materials

It has been recognized that the thermal, hydrothermal and mechanical stability of as-synthesized mesoporous template silicates is limited [21].

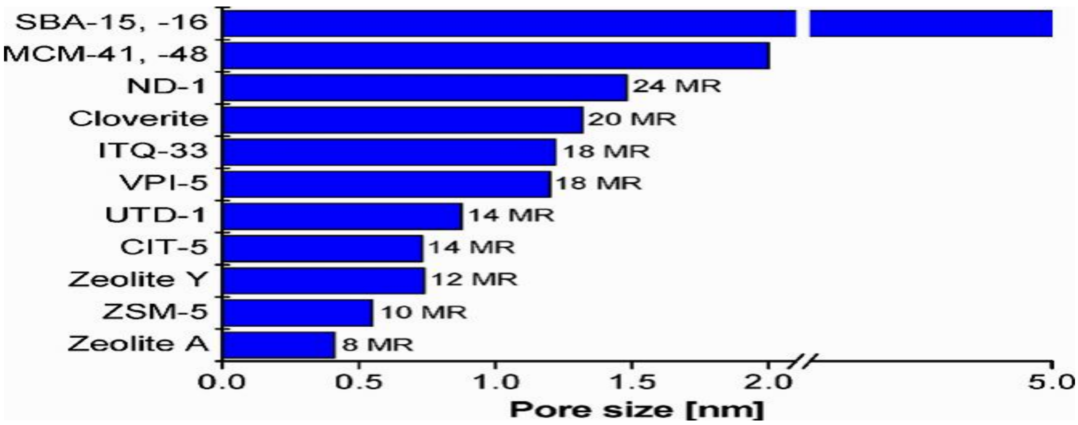

Figure 3: Pore size of different porous-tailored materials. MCM-41 and MCM-48, and SBA-15 and SBA-16 can be prepared with pore sizes up to 10 and 30 nm, respectively4.

A perfectly zeolite material, e.g. M41S (MCM-41, -48, -50) having walls of ZSM-5 or zeolite beta, would continue the increasing pore size trend established in Fig. 3. One may imagine such a zeolitized material as an extra-large pore zeolite with walls made of pentasil rings (in the case of stabilizing using the MFI-type zeolite). For this purpose, typical zeolite organic structure-directing agents can be added to the corresponding synthesis solution, and as a result nanoparticles of zeolite are found imbedded in the amorphous wall of the mesoporous material [21]. This gives rise to micro/mesoporous composites combining microporosity of zeolite units with mesoporous of amorphous phases, and to synergies in terms of properties and potential application of the new types of hierarchic materials obtained [22]

6. Conclusion

For many important applications, the size of the zeolitic pores are too small to react the bulky desired molecules the total number of ZSM-5 acid sites, as measured by TPD of ammonia. The performance of ZSM-5 as the FCC catalyst additive in gas oil cracking, since it has been proven that a direct and smooth correlation exists between the product yields and the total acidity of the ZSM-5 zeolite. The method adopted in the study resulted in the successful synthesis of nano crystalline ZSM-5 (NZ) of 30 nm range that exhibited comparable acidity with the micro crystalline one (Z). The NZ having additional porosity (mesopores created by stacked packing of nano size crystals of

ZSM-5) and strong acidity has exhibited enhanced production of gasoline rich in aromatics and branched paraffins. The ZSM-5 total number of acid sites and the aluminum content, in the case of fresh samples, or the temperature of hydrothermal deactivation in the case of steamed samples is straightforward. And HZSM-5 zeolites with varying acidity with FCC catalyst.

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