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Preparation of 5A zeolite monolith granular extrudates using kaolin: Investigation of the effect of binder on sieving/adsorption properties using a mixture of linear and branched paraffin hydrocarbons

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Abstract

5A zeolite monolith extrudates using kaolin is synthesized, and effect of binders on sieving/adsorption properties of the prepared zeolite is reported. The monolith extrudates of 4A zeolite powder produced as the precursor of 5A zeolite in the first stage of synthesis process was prepared using different percentages of kaolin powder and carboxymethylcellulose (CMC) as binding agent. The average particle size distribution of produced 4A zeolite was between 20 and 40 US standard mesh sizes equivalent to 0.841 mm and 0.420 mm, respectively. The extrudate was calcined at 600 °C, and the kaolin content of extrudates was converted to type A zeolite through ion exchange by immersing the extrudates in caustic soda solution. The 4A zeolite extrudate samples were converted to 5A type through ion exchange process using calcium chloride solution.

The 5A zeolite samples were characterized using XRD, SEM, and EDX instrumental analytic methods. Sieving test was carried out using samples of 5A zeolite and a special cut of kerosene containing C_{10}–C_{13} saturated hydrocarbons using a simple dead-end fixed bed.

Results show that the highest purity of 5A zeolite, highest rate of calcium ion exchange, and best sieving results are obtained when 30 wt% of binder (kaolin) is used, and use of small amounts of CMC as an organic binder along with inorganic kaolin binder has a profound effect on the adsorption properties of the synthesized 5A zeolite. This profound effect is attributed to de-clogging of the cylindrical pores due to CMC gasification in final calcinations of the extrudates.

Keywords: Zeolite; Binder; Ion exchange; Kaolin; Adsorption; Organic binder; Carboxymethylcellulose (CMC)

1. Introduction

Synthetic zeolites are a class of highly porous materials that have found widespread use since their advent in late 1940s and early 1950s. The unique structural features of these crystalline micro-porous solids that contain pores and cavities in the order of molecular dimensions (3–10 Å) is the main reason for their application in the realms of catalysis, separation, purification, ion exchange, radioactive waste clean-up, etc. More novel applications for zeolites are expected in electrochemistry, photochemistry, pharmaceutical engineering, membrane science and technology, and nanotechnology as their structures are expanded and more suitably engineered in a foreseeable future.

It is well established that these materials that are equivalently called molecular sieves are mainly hydrated aluminosilicates of 1A and 2A group metals of periodic table in crystalline form, with the primary structural units of SiO_4 and AlO_4 tetrahedra. These building blocks are linked together in a three-dimensional framework by shared

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oxygen atoms. The connection of these elementary building units through a common oxygen atom forms a wide variety of secondary structural units, which in turn are mutually linked to form a wide range of polyhedra. The interconnection of these polyhedra results in an inorganic macromolecule with infinitely extended frameworks of the various specific zeolite crystal structures [1–3, among others]. Chemical composition of zeolites are often and conveniently represented by

$$M^{n+}_{x/n}[(AlO^-_2)_x \cdot (SiO_2)_y] \cdot zH_2O, \quad (1)$$

where M is a cation with the charge of n, $(x + y)$ is the number of tetrahedra per crystallographic unit cell and y/x is silicon/aluminum ratio [4–6]. Based on the celebrated Löwenstein's rule [7] Al–O–Al linkages are not allowed and $y/x \geqslant 1$.

Synthesis, properties, characterization, applications, and future prospects of synthetic zeolites have been treated extensively in numerous authoritative monographs [1–6,8], and review articles [9–14]. Type A commercial synthetic zeolites possess three-dimensional pore structures and are extensively studied because of their diverse applications in industry. In principle, the synthesis of A-type zeolites is quite simple; the generic process includes the preparation of the four basic ingredients: silica, alumina, templates, and a source of seeds for the promotion of nucleation. These basic components are mixed in appropriate proportions to form a homogeneous slurry or gel, and the latter is subsequently aged under the desired pH, temperature, and pressure (e.g. [14]). Contacting a given A-type zeolite with a dilute solution of the soluble salt of the desired exchange cation will result in an exchange of cation. For instance, in the preparation of 5A zeolite Na-zeolite is exchanged by calcium cation using dilute solutions of calcium chloride at moderate temperatures. When the desired cation form is obtained in ion exchange reaction, the zeolite is blended with a binder, glue, diluent, filler, or a combination thereof, and subsequently formed into the required shape (e.g., beads, pills, tablets, or extrudates). At times for special purposes, the zeolite is spray-dried. Depending on the source and type of ingredients used, and reaction conditions a wide variety of recipes for 5A zeolite fabrication are available in open literature. As a result of research and development activities of industrialists and academicians, the number of preparation methods and fabrication processes for 5A zeolites are in the rise annually. These efforts are mostly published in the form of issued patents.

The purpose of this communication is not to review the synthesis routes available for 5A zeolites, and the interested reader can refer to the rich pool of patents issued in the last 5 decades. However, it is worth to mention that in the synthesis of zeolites the diversity of the sources of basic ingredients, reaction and physical conditions that has to be closely controlled, and thermodynamic metastablity of synthetic zeolites in their preferred synthetic conditions [14] lead into various fabrication methods and final structural and functional properties. In addition to these complications, the physicochemical and mechanical properties determined by the addition of binders in final fabrication step and zeolite forming to meet given application needs is an unresolved issue of outstanding significance.

The forming process in zeolite fabrication is still considered as an art and needs special attention in its own right. For example, very little is known about the possible effects of sequence of events of processing procedures and additives that are used on rheological behavior of the pastes that are prepared for shaping the zeolites as pellets, granules, or extrudates. Also, information on the possible effects of different additives and binders on the quality and properties of zeolites on their final shape in different applications is scarce, and effects of the utilization of these type of additives on the microstructure of the zeolite in its final shape is not studied/well understood.

This contribution is devoted to synthesize 5A zeolite and investigate the effect of using carboxymethycellulose, as an organic binder in post-processing of zeolite, on adsorption and sieving properties of the prepared monolith granules by batch adsorption of a special cut of kerosene containing C_{10}–C_{13} saturated hydrocarbons. Study of the rheological behavior of the pastes in shaping stage, and study of the effects of use of CMC on the microstructure of 5A zeolite extrudates produced in this study is subject to two other ongoing research projects. Section 2 of this paper explains materials and methods used, in Section 3 results are presented and discussed, and in Section 4 conclusions and some concluding remarks are summarized.

2. Materials and methods

2.1. Materials

Laboratory grade kaolin (Merck) was used as the supply source of alumina (Al_2O_3) and silica (SiO_2). The XRF (X-Ray Fluorescence) analysis of the used kaolin is listed in Table 1. Commercial 5A zeolite samples, called NWA-II, produced by SINOPEC Company (China) was provided by Iran Chemical Industries Investment Company (ICIIC). The bulk properties of this material are shown in Table 2. Analytical grade sodium hydroxide flakes (Merck), analytical grade calcium chloride (Houchst), medium molecular

Table 1
XRF analysis of kaolin

No.	Component	Weight percent
1	Al_2O_3	37.11
2	SiO_2	46.36
3	MgO	0.52
4	CaO	0.18
5	F_2O_3	1
6	TiO_2	0.15
7	Na_2O	0.15
8	K_2O	1.43
9	Loss on ignition (LOI)	13.1