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Adsorptive separation of meta-xylene from C_8 aromatics

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ABSTRACT

Industrial adsorptive separation process for liquids is most successful when the involved species have very close boiling points, making distillation expensive or are thermally sensitive at convenient distillation temperatures. The adsorption process was studied for separating meta-xylene from a feed mixture containing all C_8 aromatics on binder-free X and Y zeolites in the liquid phase. Zeolitic adsorbents with different SiO_2/Al_2O_3 were synthesized by the hydrothermal method and ion-exchanged with alkaline metal cations like lithium, sodium and potassium. The adsorption process was carried out in a breakthrough system at temperature of 110–160 °C and pressure of 6–8 atm. The influence of adsorbent moisture content on the separation process was studied. The optimization of adsorption process was also investigated by the changing operation conditions. The isotherms for each isomer of C_8 aromatics and the desorbent possess the adsorption characteristics of Langmuir type. The selectivity factor of meta-xylene and the saturation adsorption capacities of adsorbates were determined. It was observed that the selectivity of meta-xylene increased by sodium ion-exchanging of cationic sites in Y zeolite and the selectivity factor of meta-xylene/para-xylene, meta-xylene/ortho-xylene and meta-xylene/ethylbenzene in the optimum conditions was determined to be 2.62, 2.83 and 5.93, respectively.

Keywords: Adsorptive separation; Na–Y zeolite; Selectivity factor; C_8 aromatics

1. Introduction

The growth in demand of meta-xylene (MX) is closely linked to the demand growth of para-xylene (PX), as it is used as a co-monomer in the production of polyethylene terephthalate (PET) based packaging resins with very low oxygen permeability. MX is first oxidized to isophthalic acid (IPA) prior to copolymerization with terephthalic acid (PTA) and ethylene glycol to produce the enhanced gas barrier resins. Significant progress is being made in using MX as the primary monomer in other resins with low oxygen permeability such as meta-xylenediamine (MXDA) (Harada, 1988; Toft and Postoaca, 2002). Industrial production of MX was first accomplished by Mitsubishi Gas Chemical in the early 1980s using an HF/BF_3 ionic liquid (Kulprathipanja, 2010a,b,c,d,e). Other methods like fractionation (Berger et al., 1972), crystallization (Mohameed et al., 2007) and also extractive distillation have been proposed to recover MX from C_8 aromatic isomers (MX, PX, ortho-xylene (OX), ethylbenzene (EB)). Fractionation method is used to separate two or more solutes, by making use of their difference in solubility. Mikitenko and MacPherson (2000) reported a process for separating PX containing at least two crystallization stages at high temperature. The crystallization process consisted of two major events, nucleation and crystal growth. It was concluded that ultimate recovery of pure MX was around 99%. Hotier et al. (2008) reported a process for producing high purity MX, containing simulated moving adsorption and crystallization. In this system adsorption unit with 15 beds of adsorbent coupled with a crystallization zone which produced MX with a purity of 99.7%. Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, that forms no azeotrope with the other components in the mixture. In the process for separation of MX from a mixture containing MX and OX by extractive distillation MX was recovered in a rectification column in the presence of about one part of extractive agent. Final mixture included a vapor composition of 57.6% MX and 42.4% OX (Berg and Yeh, 1987). It has been also suggested

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to recover MX from the process streams circulating in xylene isomerization units prior to or subsequent to the recovery of other desired xylene isomers (http://www.uop.com). However, the recovery of MX has not been commercial success and much MX in these sources is simply converted to other materials such as benzene or PX. Since 1980 all new MX has been produced via the UOP MX Sorbex^{TM} process, which utilizes simulated moving bed (SMB) principles and can process a variety of C_8 aromatics feeds (Kulprathipanja, 1999). The liquid phase adsorption process is favored for its operational, maintenance and environmental advantages over the previous technologies. About 300,000 tons/year of MX capacity was constructed in the late 1990s using the MX Sorbex^{TM} process. The adsorbents of zeolite used in the MX Sorbex process are metal ion-exchanged Beta and Faujasite (FAU) type zeolites (Zinnen et al., 2000; Gomes, 2008; Minceva and Rodrigues, 2004). Kulprathipanja and co-workers reported a process for separating MX from aromatic hydrocarbons by adsorption separation method (Kulprathipanja et al., 2009). In this system the selectivity factor of MX to PX, OX and EB on sodium-exchanged zeolite Y were 2.23, 2.18 and 5.88, respectively. Leflaive and Berthelet (2007) reported the separation of MX from a mixture including MX and OX. In their research the selectivity factor of MX/OX and adsorption capacity on Na–Y adsorbent was obtained to be 1.92 and 0.186 (g/g zeolite), respectively, at temperature of 125 °C.

The framework for FAU type zeolite can be built by linking sodalite cages through double six-rings. This creates a large cavity in FAU called the “supercage” (which should really be called a supercavity) accessible by a three-dimensional 12-ring pore system (Kulprathipanja, 2010a,b,c,d,e). Zeolites X and Y are versatile molecular sieves from the faujasite family of zeolites with 7.4 Å pore size and three-dimensional pore structure (Song et al., 2005).

In the present work, for the first time effect of monovalent alkaline metal cations on zeolites X and Y (FAU structure) was investigated in the process for adsorptive separation of MX from a feed mixture containing all C_8 aromatics. Zeolites X and Y were hydrothermally synthesized, characterized and ion-exchanged with lithium, sodium and potassium cations for MX separation. Specific physical properties of zeolites such as framework structure, choice of exchanged metal cations, SiO_2/Al_2O_3 ratio and water content were manipulated in order to influence the acidity of zeolites, which in turn, affects the separation performance. Adsorption process was carried out on a breakthrough system at the desired temperature and pressure. The degree of separation was characterized by the zeolite selectivity factor, and the operating conditions such as temperature, pressure and feed rate were specified. Operation conditions and mechanism were discussed.

2. Materials and methods

2.1. *Chemicals*

The chemicals of meta-xylene (MX), para-xylene (PX), ortho-xylene (OX), ethylbenzene (EB), and isooctane (IO) were chemical grade and toluene (TB) was of analytical grade, purchased from Merck Chemical Reagent Corporation. The mixtures of hydrocarbon feed were prepared from the chemicals mentioned above to simulate the stream of the typical C_8 aromatic product from reformers. Also sodium hydroxide, aluminum trihydrate, aluminum sulfate, ammonium chloride, sodium aluminate, sodium silicate, sodium chloride, lithium chloride and potassium chloride were purchased from Fluka chemical company.

2.2. *Adsorbents preparation*

2.2.1. *Zeolite X preparation*

20 g of sodium aluminate was dissolved in 30 g de-ionized (DI) water. The solution was slowly heated up to 80 °C and maintained at this temperature. 55 g sodium silicate was slowly added to the sodium aluminate solution and stirred for 2 h (solution A). The agitator was turned off and the mixture aged for 48 h at 25 °C. 78 g of sodium silicate was diluted with 120 g DI water and the solution was mixed with 16 g aluminum sulfate solution (solution B). 10 g sodium aluminate was diluted with 10 g DI water; then it was slowly added to the silicate and aluminate mixture and was mixed (seed). After that, 2.5 g of nucleation center (seed) was added to other reactants (solutions A and B). Finally, 8 g of tetra-methylammonium chloride was dissolved in 10 g DI water and the solution was slowly added to the other component. The synthesis gel was poured in the Teflon-lined stainless steel autoclave and slowly heated to 80–100 °C for 48–72 h. Then, the content of autoclave was filtered in the Buckner funnel and it was washed with distilled water until the filtrate had the pH of about 9. The materials were dried at 110 °C overnight. The X-ray diffraction pattern showed that it contained 99% zeolite X. The synthesized zeolite was changed to the ammonium form by ion-exchanged method using ammonium chloride 10% at 80 °C followed by sodium chloride 10% at 80 °C (Hu and Hiimatta, 1996; Priegnitz et al., 2010; Masini and Plee, 2004).

2.2.2. *Zeolite Y preparation*

100 g of sodium hydroxide was mixed with 300 g distilled water until being dissolved. 97.5 g aluminum trihydrate was dissolved in the sodium hydroxide solution which was previously heated to 100 °C. 100 g of the prepared solution was mixed with 612 g distilled water and 59 g of sodium hydroxide until being dissolved (solution A). The solution of 220 g sodium silicate was slowly added to the solution containing 59 g sodium hydroxide and 612 g distilled water; then, were mixed until being dissolved (solution B). Solution A was slowly added to solution B and mixture was well agitated for 30 min. The solution was transferred to a stainless steel autoclave lined with PTFE (Teflon) and kept in a static air oven at 80–100 °C for 48–72 h. The crystalline material was separated by filtration and washed with distilled water until the pH was neutral ($pH < 10$). Finally, the materials were dried at 100 °C. The product was analyzed by X-ray diffraction and found to be 99% zeolites Y. The synthesized zeolite was changed to ammonium form by ion-exchange method using ammonium chloride 10% at 80 °C followed by sodium chloride 10% at 80 °C (Sanders, 1984; Weber, 1974; Elliott and McDaniel, 1970).

2.2.3. *Ion-exchange by monovalent cations*

There is a strong correlation between the total acidity of a zeolite (the sum of both Brönsted and Lewis acids) and the ionic radius of the cations as well as the valence charge of the exchanged cations (Barthomeuf, 1996; Seko et al., 1979). For FAU zeolites, the aluminosilicate structure is a three-dimensional open framework of AlO_4 and SiO_4 tetrahedrals linked to each other by oxygen molecules. The framework contains channels and interconnected voids occupied by cations and water molecules. The cations are mobile and can be