Synthesizes of Ion-Exchange Resins as MTBE Production Catalyst

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Abstract: Ion-exchange resins are used as catalyst in production of MTBE. The catalyst are used in various forms. Catalytic packing is one of these forms that can be in different shapes and sizes. As a part of a research study, the resin is synthesized by copolymerization of styrene and divinylbenzene. The polymerization process is carried out under various selected conditions. Various properties of the produced catalysts such as acidic capacity, swelling ratio, porosity, effective beads size and density are measured. The effects of reactant monomer concentration and various stabilizers on efficiency and quality of product are tested. The most comparable produced resins to the commercial ones from surface properties point of view, acidity and morphology, are used for production of various types of catalyst packing implementing sol-gel technology.

Keywords: Ion-exchange resin, MTBE, Catalyst, Polystyrene-divinylbenzene

Introduction

Ion-exchange resins are used widely in various processes. Water treatment and process of Methyl-Tert-Butyl-Ether (MTBE) production are just two of them. Catalytic distillation is an interesting process for production of MTBE due to its high efficiency and simplicity. Combination of two simultaneous processes of chemical reaction and distillation reduces the requirement to operational equipment, energy and consequently overall costs. In this process sulfonic type of ion-exchange resins are used as catalyst. The catalysts are implemented in various forms such as sewn the beads of resins into a wire net, the beads filled in glass fiber fabric called bales and catalytic packing in different sizes and forms of packing such as ceramic bales, rasching rings, berl saddles and structured aluminum packing. The ion-exchange resins have a polymeric structure. These resins are insoluble in water due to existence of cross-link in their polymer matrices. But, they are hydrophilic and solution ions can penetrate into the resins' pores. The structure of resins must be chemically stable under various operational conditions. The catalytic properties of these materials are due to existence of ionic-exchange groups over their surfaces (Akbarnejad *et al.*, 2000; Gates and Rodrigues, 1973; Mehrabani-Zeinabad, 2002; Rehfinger, 1998).

The catalytic agent of these resins is acids/bases that are used during their production process. The catalysts are generally produced by copolymerization of styrene and divinylbenzene as a source of cross-linking. These catalysts are in hydrogen form of sulfonic acid or hydroxide form of ammonia. There are two categories of these catalysts, gelular and macroreticular. The

gelular ion-exchange resins regardless of its name are in form of hard, transparent and spherical beads. Their structure is destroyed as they become dried. These resins require a swelling agent for enhancing their catalytic characteristics. The agents expand the polymeric matrix by generation of spaces between polystyrene chains. The micro-porous spaces are passing paths for reactive components that indeed cause resins' catalytic characteristics. In gelular type of resins, the amount of cross-linking is less than 12%. Higher cross-linking results in lower catalytic property due to increasing resistance of ion diffusion. This issue reduces available spaces on the resin surfaces for the ion-exchange process (ROHAM and HAAS, 1980).

The macroreticular ion-exchange resins have a heterogeneous structure. These resins do not require the swelling agent for acting as catalyst. The amount of cross-linking in this type of resins could be increased up to 50%. This type of ion-exchange resins has general and industrial benefits. Some of them are (Akbarnejad *et al.*, 2000) simplicity in its transportation, storage and distribution, (Dorfner, 1962) implementing as catalyst for both batch and continuous reactors, (Dow Chemical Co., 1992) reducing environmental pollution, (Gates and Rodriguez, 1973) reducing reactor corrosion and (Kunin *et al.*, 1962) easy and fast separation from the reaction products (Kunin *et al.*, 1962).

Ion-exchange resins can be classified in three groups of cationic, anionic and electronic. Chemical companies supply these resins for various applications under different brands and commercial names. AMBERLYST-15 resin produced by ROHM& HASS Co. is one of these resins that can be used as catalyst for production of MTBE. Physico-chemical properties of this resin are shown in Table 1. The resin is synthesized by suspension copolymerization of styrene and divinylbenzene. This method of production in comparison with the bulk method generates more uniform resin beads. Production of polymer in bulk and palletizing of the produced polymer reduces polymer strength and causes non-uniformity in sizes and granulites of the polymer beads. In this study sulfonic acid type of ion-exchange resins are synthesized as catalyst of MTBE process (Fig. 1). The synthesized resin is used for production of various types of catalytic packing by implementing sol-gel technology (Mehrabani-Zeinabad *et al.*, 2002; Stiles, 1987).

Materials and Methods

The sulfonic acid type of ion-exchange resins are synthesized by using the following chemicals from Merck Co., styrene, divinylbenzene (with a purity of 65%), benzoyl peroxide, normal hexadecane and concentrated sulfuric acid. A set of experiments is done and information of some experiments is shown in Table 2. Initially at room temperature the mentioned amount of distilled water is poured into one-liter batch reactor. Then the certain amount of suspension agents of carboxymethyl cellulose (CMC) or polyvinyl alcohol (PVA) is added. In the next step styrene, divinylbenzene and benzoyl peroxide are included in the reactor mixture. The divinylbenzene acts as the polymer cross-linking agent. By increasing the polymer cross-link, swelling property of the resin is increased greatly. This enhances the resins' lifetime. The benzoyl peroxide is the polymerization initiator. The normal hexadecane is a pore-forming agent.

Table 1: Physico-chemical Properties of Catalyst   AMBERLYST-15 (Roham and Haas Co, 1980)

Type	Strong acid cationic ion-exchange
Ion-type	H^+
Humidity	51-56%
Bead size	0.3-1.2 mm
Effective size	0.51-0.61 mm
Acidic site concentration	1.8 meq/ml
Area	50 m^2 gr^{-1}
Porosity	0.42 ml gr^{-1} dry resin
Pore diameter	24 nm
Bulk density	0.76 gr ml^{-1}

Table 2: Ion-exchange synthesis data and conditions

Sample #	Styrene (gr)	Divinyl benzene (gr)	Water (gr)	Addec Additives	Temperature (°C)	Time (Hr)	Agitator Speed (rpm)	Reflux Time (min)
MTM-01	100	10	-	1gr BP*	65	24	-	-
MTM-02	95	5	300	1gr BP	90	3.5	200	30
MTM-03	95	5	300	1gr BP 3gr CMC**	90	3.5	200	30
MTM-04	95	5	300	1gr BP 3gr CMC 5gr NH***	90	3.5	200	30
MTM-05	95	5	400	1gr BP 3gr CMC 5gr NH	90	3.5	1400	30
MTM-06	95	5	200	1gr BP 3gr CMC 5gr NH	90	3.5	1400	30
MTM-07	80	20	400	1gr BP 3gr CMC	90	3.5	1400	30

* BP :: Benzoyl Peroxide; ** CMC :: CarboxyMethyl Cellulose; ***NH :: Normal Hexadecane

The mixture is agitated with the mentioned rate. Agitation rate has a great influence on diameter of the produced resin beads, as the rate increases the diameter decreases. The temperature is increased to 90°C for a period of 3.5 h. For a period of 30 min the reflux operation is carried out. The produced mixture is cooled and filtered. The synthesized copolymer beads are dried at temperature of 125°C for a period of 6 h.

In the next step, for synthesizing of cationic ion-exchange resin the dried beads of styrene-divinylbenzene copolymer are mixed with 100 cubic centimeter of concentrated sulfuric acid. The sulfonation process is done at temperature of 100°C for a period of 8 hours. The mixture is cooled and then is washed for removal of used acid. The following tests are carried out in order to measure the catalyst properties.

Measurement of acidic capacity and solid content

Catalytic properties of resins depend on their SO_3H groups. The important property of acidic capacity is measured based on titration method. Initially about 5 g of the resin is mixed with one liter of nitric acid. This operation generates the hydrogen form of the resin. Then, the resin is washed and dried. In the next step, one gram of the resin is added to 200 cubic-centimeter of standard 0.1 molar of sodium hydroxide solution. The mixture is hold for one night. The remaining resin is used for measurement of solid content. In the next step, 50 cubic centimeter of the liquid is tittered with standard acid of 0.1 normal. The amount of tittered acid is used for calculation of acidic capacity.

For measuring of solid content, a certain weight of the resin is kept in a 110°C furnace for one night. The remaining solid is weighted and based on it the solid content percentage can be calculated.

Measurement of density

By using a measuring cylinder, a certain volume of it is separated. Then, the mass of sample is measured. By dividing of the measured mass and the measured volume, the bulk density of the catalyst can be determined. In order to obtain the beads density, the porosity of the catalyst must be considered. For this issue, an inert liquid such as distilled water can be used. The volume of used liquid for filling the free space among the catalyst beads is measured, the porosity volume. The difference amount of the catalyst and the porosity volumes is the beads volume. This is used for calculation of the beads density. These tests are done for sample MTM-05 and the results are shown in Table 3.

Table 3: Properties of the produced catalysts

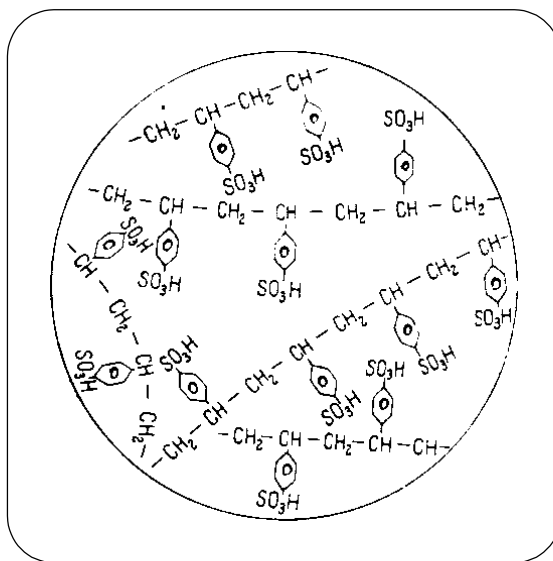| Sample #	Effective Beads Size (mm)	Porosity (mlit gr^{-1})	Cross -linking (%)	Spherical Factor	Acidic Concentration (meq/gr)	Beads Density (gr ml^{-1})
MTM-01	Bulk	0.1	9	-	4.6	-
MTM-02	8-12	-	5	1.6	4.8	-
MTM-03	8-12	-	5	1.4	4.8	-
MTM-04	8-12	-	5	1.4	4.8	-
MTM-05	0.5-1.2	0.38	5	1.2	4.8	1.17
MTM-06	20-30	-	5	1.7	4.8	-
MTM-07	0.5-1.2	0.41	20	1.2	4.1	-

Fig. 1: A schematic view of sulfonic acidic ion-exchange resins

Measurement of catalyst porosity and spherical factor

Porosity of the catalyst is measured by QUANTASORB instrument, from QUANTACHROME Co. based on Brunauer-Emmett-Teller (BET) method using nitrogen and helium gases. The test results for samples MTM-05 and MTM-07 are shown in Table 2. Also for the above samples the variation of catalyst porosity is measured in some time interval during the polymerization process. These data are shown in Fig. 2.

Spherical factor of the produced beads is calculated by implementing electronic microscope and following formula.

$$\text{Spherical Factor} = \frac{(\text{Bead Perimeter})^2}{(\text{Bead Surface Area}) \times 4}$$

The spherical factor is equal to one for a sphere bead.

Measurement of catalysts' effective area

The effective areas of the produced catalysts are measured by Quantasorb instrument implementing BET method. Also effective area of the produced catalysts with respect to polymerization time is shown in Fig. 3 for some time interval.

Determination of the polymer cross-link bonds

The percentage of polystyrene-divinylbenzene cross-link bonds is calculated based on the following formula.
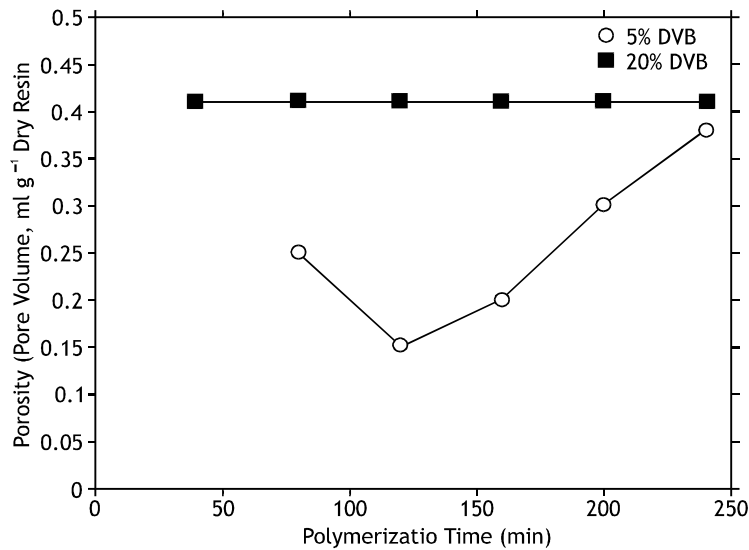

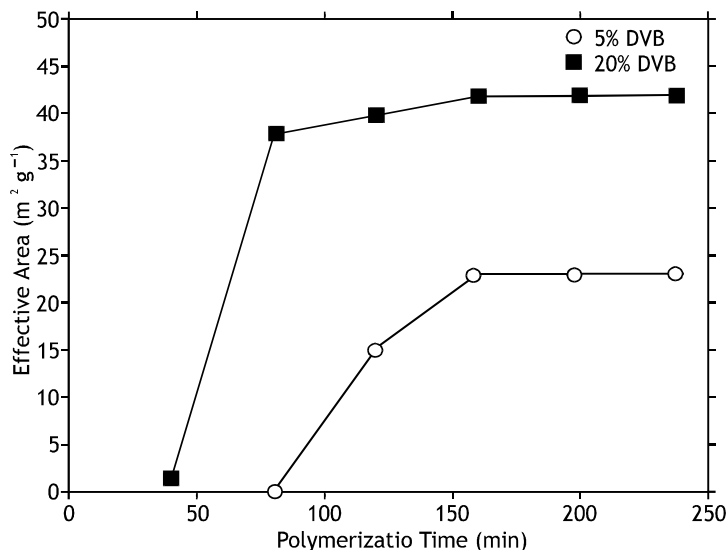Fig. 2: Variation of ion-exchange resin porosity in polymerization period

Fig. 3: Variation of effective areas in polymerization period

$$\text{Cross Link \%} = \frac{\text{(Divinyl benzene mass)}}{\text{(Divinyl benzene mass + Styrene mass)}} \times 100$$

Results, Discussion and Conclusion

Variations of pore volumes for the produced catalysts with respect to polymerization time are shown in Fig. 2. For sample MTM-07 that its divinylbenzene content is 20%, the initial porosity is 0.41 ml for a gram of dry resin. This value remains constant through the polymerization period, due to covering of the resin surface with a large amount of divinylbenzene. In sample MTM-05 (5% divinylbenzene), initially direct chains of polymer are extended with vinyl groups for synthesis of the macroreticular resin. In the next stage, by progressing of polymerization process, cross-link bonds are formed. This increases the molecular weight of the produced polymer. Thus, the porosity is reduced initially. But, by progress of polymerization process, the porosity is increased to value of 0.38 ml per gram of dry resin.

As shown in the Fig. 3, for sample MTM-07 the effective area of resin is increased form initial value of 1.5 m^2 gr^{-1} to 38 m^2 gr^{-1} in a period of 20 minutes. After this sharp increase, the effective area is increased slowly to the final value 42 m^2 gr^{-1}. For sample MTM-05 the effective area was less than 1 m^2 gr^{-1} for the first 90 minutes. But, similarly the effective area is increased to its final value due to formation of macroreticular resin. Table 3 shows various properties of the produced catalyst samples.

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