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Green catalytic Polymerization of Styrene in the Vapor phase over Alumina

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Abstract

In the present work, a new technique for the polymerization of styrene in vapor phase without any added solvent is proposed. The acidic and basic alumina was used as heterogeneous catalysts in this reaction. These catalysts were packed in the vapor phase reactor and the styrene vapor was allowed to pass through the catalytic bed at various temperatures. Both anionic and cationic polymerizations have been carried out in the presence of acidic Al_2O_3 and basic Al_2O_3 respectively. Beyond using various hazardous solvents and catalysts in the styrene polymerization reactions, the new vapor phase polymerization technique provides a right way to carry out the polymerization reactions in an environmental friendly method. The optimization of various experimental conditions like effect of contact time, temperature, monomer dosage, catalyst dosage and time on stream have also been investigated for maximum conversion of both catalysts. The resulting polystyrene structure was confirmed by FTIR spectral analysis. The molecular weight of the polystyrene was determined at various polymerization temperatures. The high molecular weights of $3.1x10^5$ and $2.8x10^5$ were obtained for acidic and basic alumina respectively at 150°C.

Keywords: Styrene, vapor phase polymerization, polystyrene, acidic alumina, basic alumina

Introduction

Some of the polymers generally have commercial application[1-7]. The synthesis of polystyrene has gained much interest in the last decade especially in catalyst and polymerization research. It leads to a fast commercialization of this product. In recent years, polystyrene was synthesized by numerous synthetic procedures such as free radical, cationic and anionic, emulsion and homo polymerizations. In all the typical synthesis, catalyst, cocatalyst, initiator and solvents play a vital role. Living and controlled radical polymerization of styrene using coordinated catalysts with halide initiator is also reported[8-12]. The catalyst bpy/Cu(I)/Cu(II) is used in living radical polymerization initiated by Arenesulfonyl chlorides[13,14]. The radical polymerization of styrene is controlled by iron complexes using a variety of coordinating ligands[15]. Room temperature ionic liquids (RTILs) also contributed as a promising reaction media for the free radical and anionic polymerization of styrene[16,17]. According to Szwarc, living anionic polymerization of styrene is attained by sodium naphthalenide in the presence of THF as catalyst[18,19].

Recently, the living cationic polymerization of styrene is reported using titanium tetrachloride and alkyl aluminum halides as co-initiators[20,21]. Silica-supported copper triflate is utilized as a heterogeneous catalyst for cationic polymerization of styrene[22]. Mesoporous silica supported aluminum chloride catalyst is prepared and used as heterogeneous initiators for cationic polymerization[23]. Normally in cationic and anionic polymerization of vinyl monomers, both rate and molecular weight were much lower at room temperature. These considerations limited the industrial applications of this type of polymerizations[24]. Also, in most of the synthetic procedures, solvents like toluene, THF, cyclohexane, benzene, ethylbenzene, diethylbenzene served as a focal participant in the polymerization of styrene[25,26]. In all the reported polymerization techniques, the separation of the polymer from the catalyst, solvent etc. was very risky and expensive process.

To overcome these problems, the novel vapor phase polymerization technique is adopted over alumina in the vapor phase. In this method, there are no hazardous solvents, initiators and catalysts are used and polymer with high molecular weight $3.1x10^5$ and $2.8x10^5$ are easily achieved at 150°C. Moreover, alumina is not yet used as catalyst for vapor phase organic reactions including polymerization of styrene. Hence, in the present work, the styrene polymerization reaction is studied over acidic and basic alumina in vapor phase.

Material and Methods

Characterization of catalysts: FTIR spectra of acidic and basic alumina were recorded with a Jasco FTIR-410 spectrophotometer in the range 4000–400 cm^{-1} using KBr pellet technique. About 15 mg of the sample was pressed into a self supported wafer of 13mm diameter.

Activation of catalyst: The acidic and basic alumina were obtained from Loba chem. Both catalysts were activated by heating in a hot air oven kept at 200°C for 3 hours. The activated acidic and basic alumina were employed for styrene polymerization.

Synthesis of polystyrene in vapor phase: For the synthesis of polystyrene in vapor phase, a fixed-bed vertical flow type reactor made of quartz tube with 40 cm length and 1.5 cm internal diameter was used. The reactor set up is shown in figure-1. The quartz reactor was heated to the required temperature with the help of a tubular furnace controlled by a digital temperature controller with an indicator. About 1 gm of acidic/basic alumina was placed in the reactor and supported on either side with a thin layer of quartz wool. The reactant styrene was fed into the reactor through the syringe infusion pump that can be operated at different flow rates. The bottom of the reactor was connected to a coiled condenser and a receiver in which the polymer was collected. The collected polymer with monomer was distilled to separate polymer from the monomer.

Optimization of Experimental conditions: In the vapor phase polymerization of styrene, optimizations of experimental conditions such as effect of polymerization time, polymerization temperature, styrene flow rate, catalyst dosage and time on stream were optimized for the maximum conversion of styrene.

Characterization of Polystyrene: Fourier transform infrared (FTIR) spectrum of polystyrene was recorded on Jasco FTIR-410 spectrophotometer at spectrum range of 4000-400cm^{-1} with a resolution of 2 cm^{-1} using the KBr method.

Conductivity measurement of Polystyrene: Conductivity of polystyrene was measured in a collinear four probe set-up (inter-probe spacing = 2mm) by drawing current from a constant power supply unit (Scientific Equipment and services, Roorkee, Model DFPO2).

Determination of Molecular weight of Polystyrene: The molecular weight of polystyrene was determined by Ostwald's Viscometer at 25°C. The polystyrene (0.2g) was dissolved in 10ml toluene. The flow time of the solution was noted to six times at 25°C. The average flow time was used for the molecular weight calculation using the following equation -1[27].

$$\frac{\eta}{\eta_1} = \frac{t}{t_1} \qquad \text{------(1)}$$

η - Viscosity of the polystyrene, **η_1** - viscosity of toluene, **t**- Time interval for polystyrene solution flow, **t_1** - time interval for toluene flow

The Molecular weight was determined by substituting this flow time in the following equation - 2.

$$M^{\alpha} = \frac{\eta}{k} \qquad \text{------(2)}$$

where M= molecular weight, α (0.63), k (3.80 X10^{-5}) are constants.

Results and Discussion

Characterization of acidic and basic alumina: The FTIR spectra of acidic and basic alumina are shown in figure - 2 (a and b). A peak at 1605 cm^{-1} is attributed to the Al-O-Al asymmetric stretching. The corresponding symmetric stretching vibration is observed at 606cm^{-1}. It is confirmed that both acidic and basic alumina have no tetrahedral framework. The strong peak at 3640 cm^{-1} for acidic alumina is due to Al---O-H stretching[28] whereas in basic alumina the broad peak at 3455 cm^{-1} is attributed to the OH stretching mode[29].

Optimization of experimental conditions: Effect of time on styrene polymerization: The polymerization of styrene over acidic and basic alumina in the vapor phase at 200°C with the flow rate of 10 ml/hour is investigated up to 4 hours to find the time effect for maximum conversion of styrene. The time effect for the styrene polymerization is shown in the figure-3a.

The percentage of conversion increased with the increase of time and attains a maximum conversion at the third hour. This may be due to the continuation of propagation of polymerization reaction from 1 to 3 hours. The conversion is 50% at 1 hour, indicates that the initiation required long time for the polymerization reaction. The conversion of styrene at third hour is 100% and remained as such for the fourth hour. This shows that all the monomer units are involved in the polymerization.

Effect of temperature on styrene polymerization: The temperature effect of styrene polymerization reaction over acidic and basic alumina is given in the figure-3b. The temperature has been examined from 100-300°C. The conversion of styrene is increased from 100-200°C and decreased the conversion with further increase of temperature. This investigation proved that the most favorable temperature for the maximum conversion of styrene is 200°C. The conversion increases rapidly from 100-200°C and further increase of temperature up to 300°C not much influences the polymerization reaction. This reveals that the styrene molecules traverse through the catalytic bed without any interaction with the active sites of the catalyst above 200°C. This may be due to the high velocity of styrene above this temperature**.**

Effect of monomer dosage on styrene polymerization: The flow rate has been studied over acidic and basic alumina from 10 ml/hour to 30 ml/hour in the vapor phase which is shown in figure-3c. The conversion is high at the flow rate of 10 ml/hour and further raise of flow rate decreased the conversion. This may be due to the over dosage of monomer, which has been passed through the catalytic bed without interacting with the active sites present on the surface of both alumina catalysts.

Effect of catalyst dosage on styrene polymerization: Catalyst dosage from 1g to 5g on styrene polymerization over acidic and basic alumina in the vapor phase at 200°C with the monomer flow rate of 10 ml/hour has been studied to find out the linear relationship between the active sites present on the surface of the catalyst and styrene conversion. This linear relationship effect on polymerization is shown in figure-3d. In this investigation, the percentage of conversion of styrene increased with the increase of catalyst dosage. This clearly confirmed that the styrene conversion has a linear relationship with the catalyst dosage. When the dosage of the catalysts is increased, the active sites and the surface area of the catalysts are also increased. Hence, the conversion of styrene is increased with the increase of catalyst dosage.

Effect of time on stream on styrene polymerization: The time on stream of styrene polymerization over acidic and basic alumina at 200°C at the flow rate of 10 ml/hour in the vapor phase are shown in figure-3e. This process has been studied for 5 hours and observed that the catalysts are constantly active up to 5 hours.

Mechanism of polymerization of styrene over acidic and basic alumina: The schematic representations of cationic and anionic polymerization of styrene over acidic and basic alumina are shown in figure-4a and 4b respectively. This markedly illustrates the initiation, propagation and termination of the reaction. In the initiation step of the cationic polymerization reaction of styrene, the H^+ ion bounds on acidic alumina, initiates the reaction and the carbocation on styrene molecule propagates the polymerization. In an anionic polymerization, the OH^- ion on basic alumina provokes the reaction and the carbanion formed on styrene molecule attacks the second monomer and propagates the polymerization. In the termination step, the long chain polymer was released from the active sites of the catalysts due to its high molecular weight and so, the either side of the long chain polymer possesses positive and negative charges. This is confirmed by the zero conductivity (± 0V) of the polystyrene which provide the evidence for the termination of the reaction.

Temperature effect on molecular weight of polystyrene: The molecular weight of the polystyrene is determined at various temperatures in order to measure the molecular weight changes at various polymerization temperatures. In figure–5, the molecular weight of polystyrene is found to be maximum at 150°C and further raise in temperature decreases the molecular weight. This reveals that at lower temperature, more number of monomers is allowed to contact in the propagation step. Further observations predict that the decrease of molecular weight with the raise of temperature is due to the high velocity of styrene molecules in the vapor phase, which reduced the number of monomers contributed in the propagation step of polymerization reaction.

Characterization of polystyrene: The FTIR spectra of polystyrene over acidic and basic alumina are shown in Figure-6 (a and b). The stretching vibrations of both the spectra are identical. The phenyl nucleus skeletal vibrations are observed from 1450 to 1600 cm^{-1}, C-H vibrations are observed from 700 to 1000 cm^{-1}, aliphatic and aromatic C-H stretchings are observed from 2850 to 3050cm^{-1}, CH_2 vibration is observed at 1250 cm^{-1} [30]. From the FTIR spectra, it is confirmed that the polystyrene is formed in the vapor phase polymerization of styrene.

Conclusion

The polymerization of styrene over acidic and basic alumina is investigated in the vapor phase. The experimental conditions like effect of contact time, temperature, monomer dosage, catalyst dosage, time on stream are optimized for maximum conversion.

The contact time for the vapor phase styrene polymerization is examined and the conversion attained a maximum at 3 hours. In the temperature study, the maximum conversion of styrene in the vapor phase is observed at 200°C. Moreover, further increase of temperature up to 300°C decreases the styrene conversion. The optimum monomer dosage on vapor phase polymerization of styrene is 10 ml/3hours for 1g of catalyst. The catalyst dosages exhibit a linear relationship on styrene conversion. The time on stream study proved that the conversion increased up to 5 hours. The high molecular weight $3.1x10^5$ and $2.8x10^5$ are obtained for polystyrene at 150°C over acidic and basic alumina respectively. Further increase of temperature up to 300°C decreases the molecular weight of polystyrene over acidic and basic alumina in the vapor phase.

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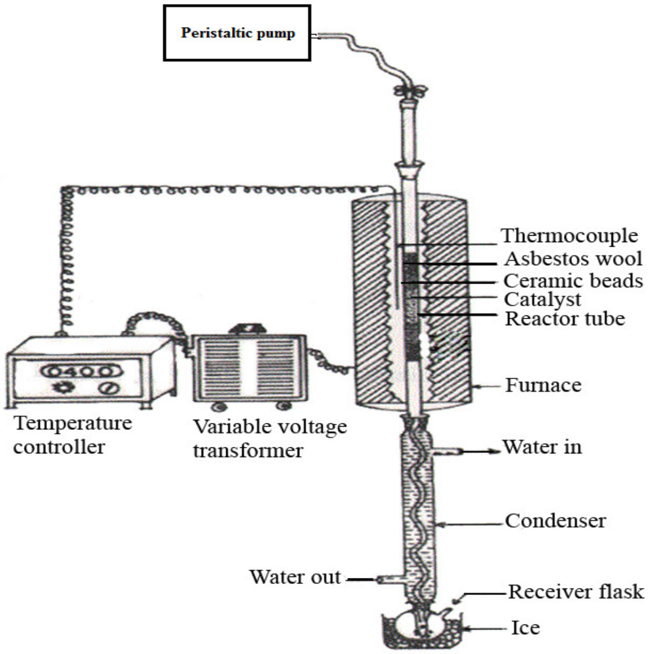

Figure-1
Vapor phase reactor

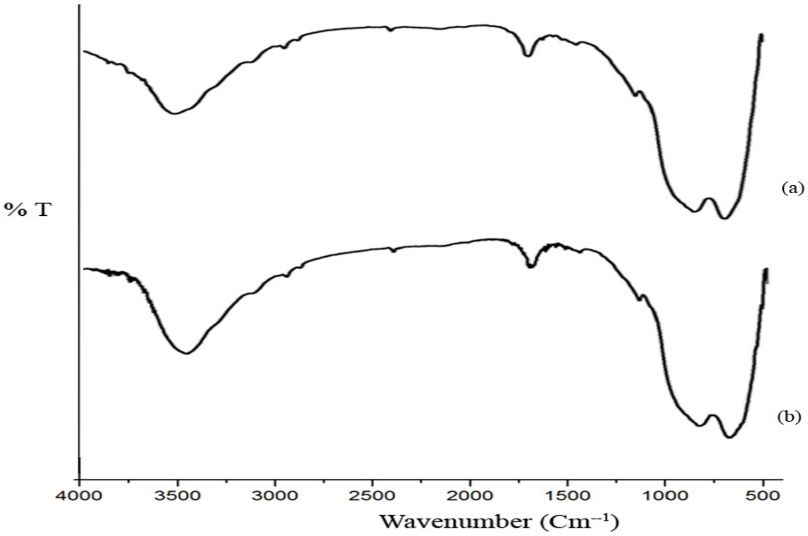

Figure-2
FTIR spectra of (a) acidic alumina (b) basic alumina

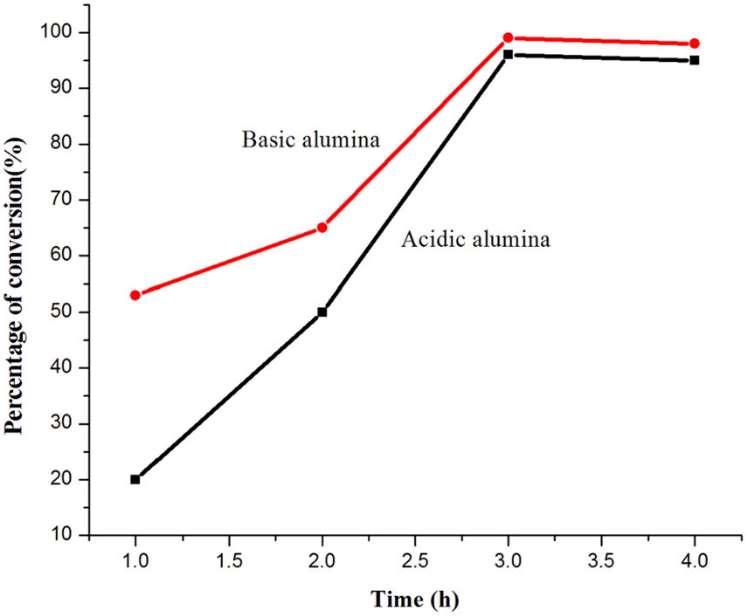

Figure-3a
Effect of contact time on vapor phase polymerization of styrene over acidic and basic alumina Reaction conditions: Monomer dosage 10 ml/hour, 200°C, amount of catalyst 1g

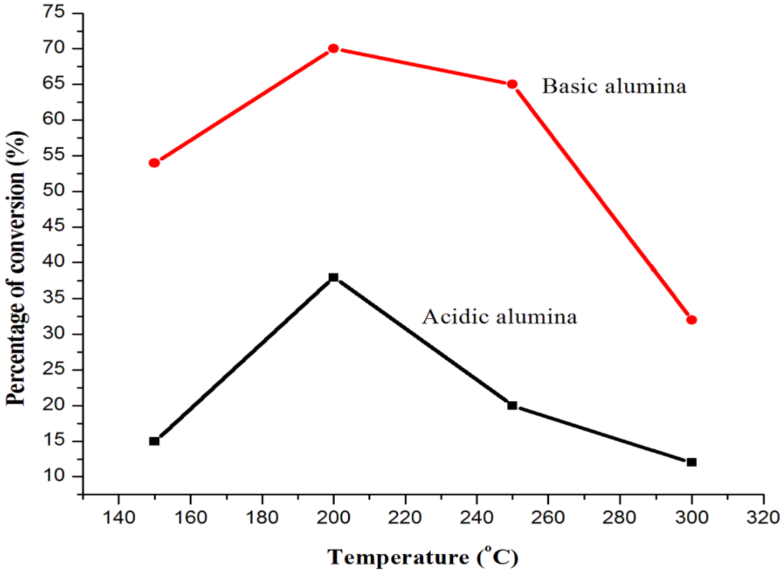

Figure-3b
Effect of temperature on vapor phase polymerization of styrene over acidic and basic alumina Reaction conditions: Monomer dosage 10 ml/hour, amount of catalyst 1g

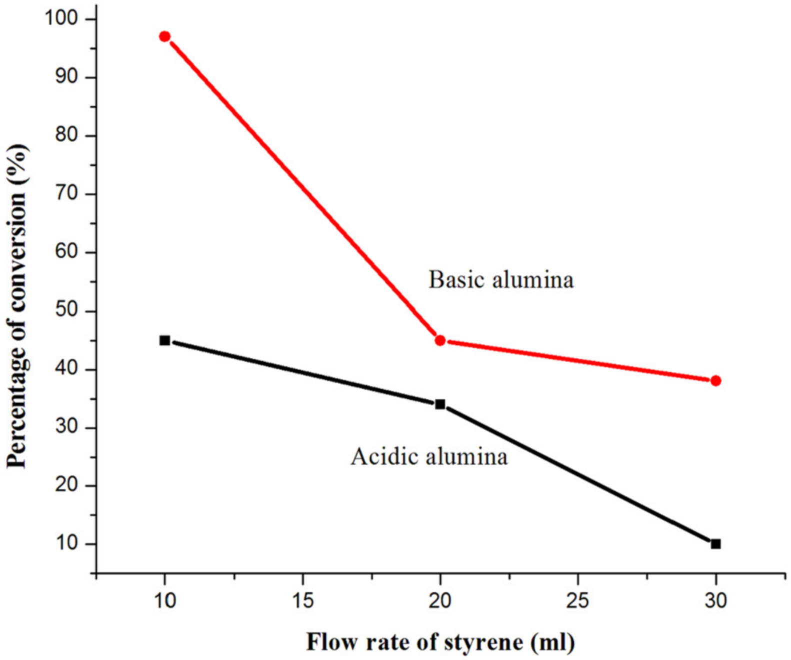

Figure-3c
Effect of monomer dosage on vapor phase polymerization of styrene over acidic and basic alumina Reaction conditions: Time 3 hours, 200^{o}C, amount of catalyst 1g

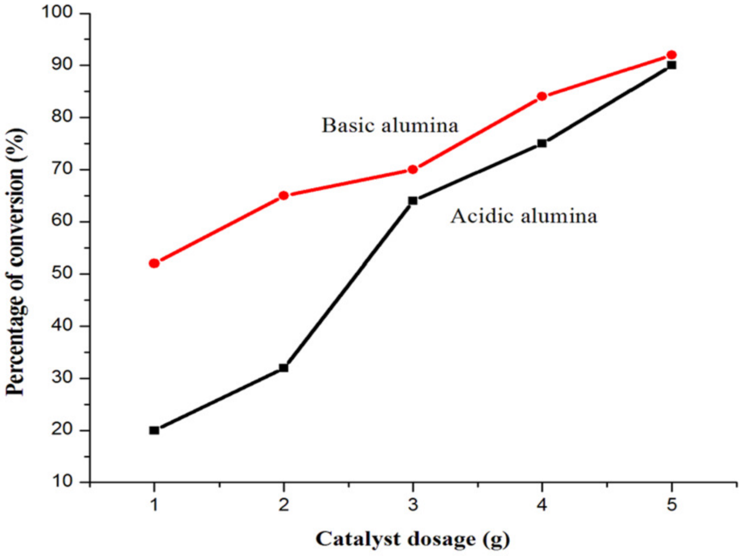

Figure-3d
Effect of catalyst dosage on vapor phase polymerization of styrene over acidic and basic alumina Reaction conditions: Monomer dosage 10 ml/hour, 200^{o}C

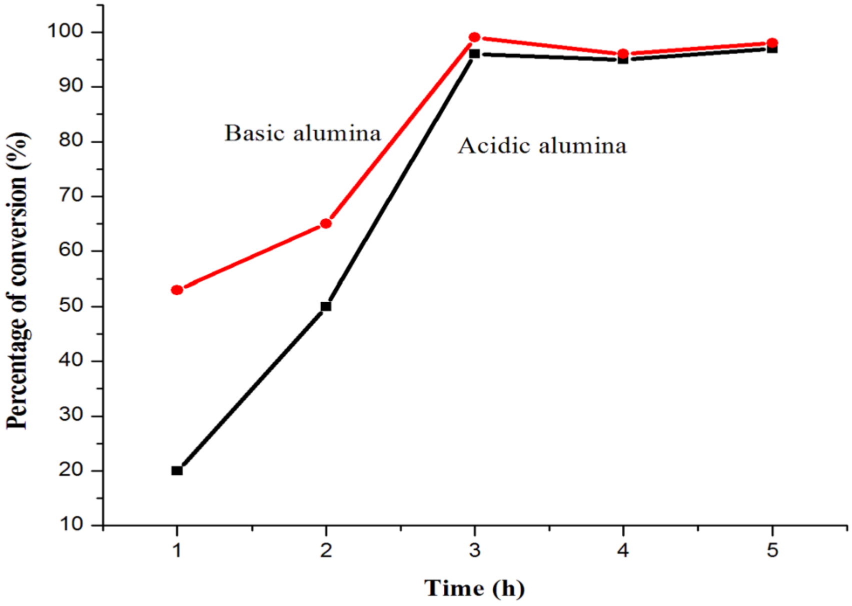

Figure-3e
Effect of time on stream on vapor phase polymerization of styrene over acidic and basic alumina Reaction conditions: Monomer dosage 10ml/hour, 200°C, amount of catalyst 1g

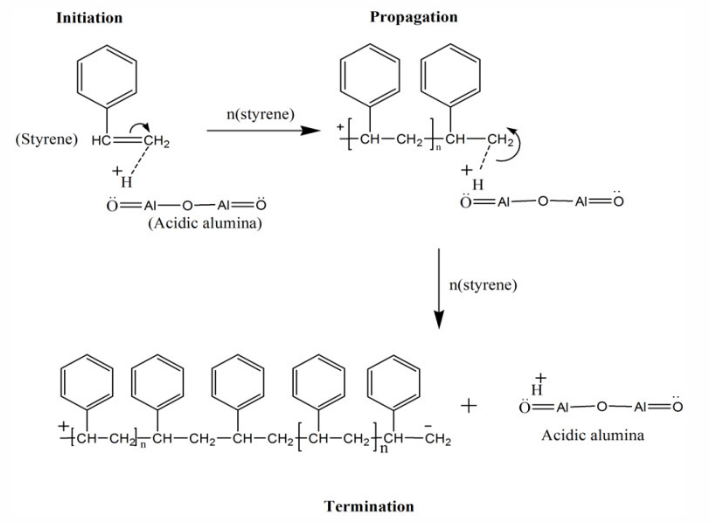

Figure-4a

Schematic representation of cationic polymerization of styrene

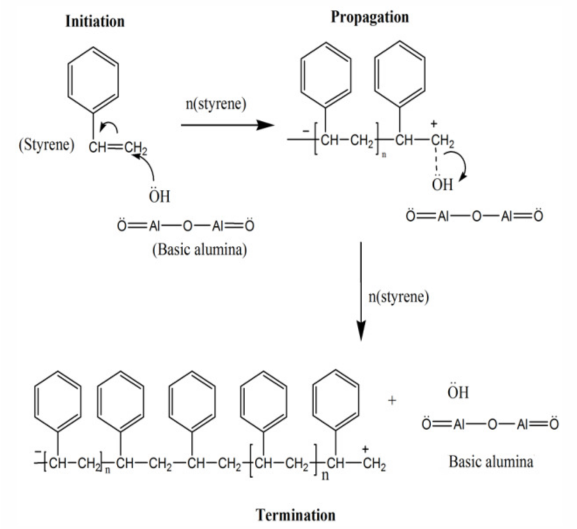

Figure-4b

Schematic representation of anionic polymerization of styrene

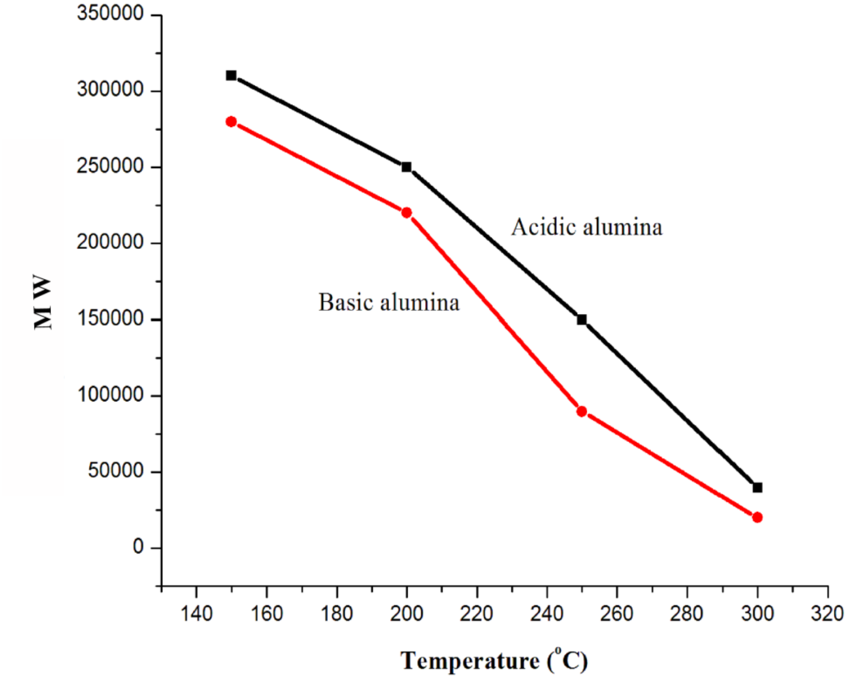

Figure-5
Dependence of molecular weight on temperature in the vapor phase polymerization of styrene over acidic and basic alumina. Reaction conditions: Monomer dosage 10ml/hour, amount of catalyst 1g

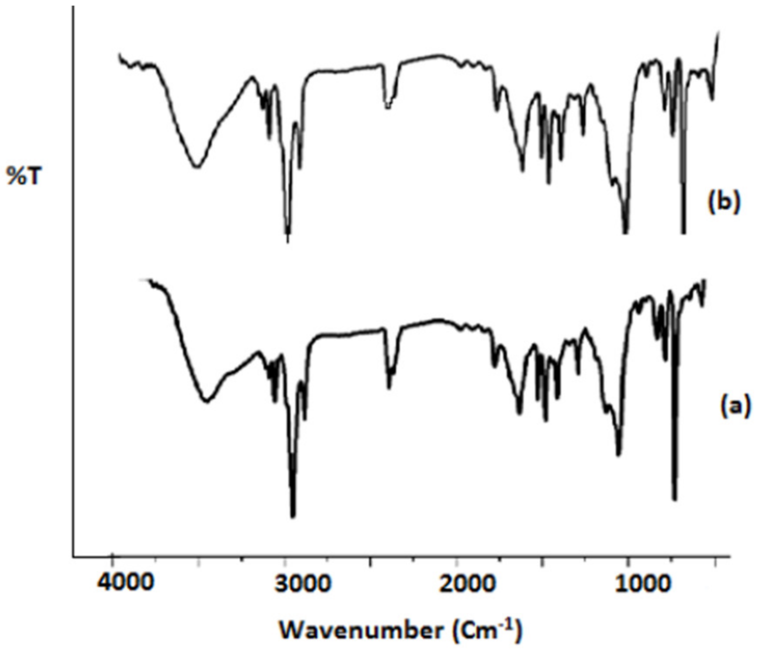

Figure-6
FTIR spectra of polystyrene (a) acidic alumina as catalyst (b) basic alumina as catalyst