# Cationic polymerization of styrene using mesoporous silica supported aluminum chloride

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## Abstract

Mesoporous silica supported aluminum chloride catalysts have been prepared and used as heterogeneous initiators for the cationic polymerization of styrene. Faster reactions with an improved control over molecular weight were obtained compared to the homogeneous Lewis acid. The concentration of silica surface hydroxyl groups has proven to have a major influence on the initiation and transfer reaction rate and on the polymer molecular weight as they act both as co-catalyst in the initiation process with the Lewis acid and as possible terminating agents. The importance of the support pore size and active center loading on the activity of the catalyst and on the polymer molecular weight have also been examined in detail. Studies on catalyst reuse are also reported.

## 1. Introduction

Cationic polymerization is a widely used method for preparing hydrocarbon polymers [1]. Numerous examples of the polymerization of vinyl monomers by a cationic pathway using various Lewis acids such as AlCl$_3$ [2,3], BF$_3$ [4], SnCl$_4$ [5,6] and TiCl$_4$ [7,8] catalyst systems can be found in the literature. These homogenous polymerization reactions are fast and efficient, using cheap catalysts, but molecular weight control is generally poor. Moreover, these homogeneous Lewis acid catalysts present some major drawbacks: their corrosive nature makes them difficult to handle and they are difficult to separate from the reaction products. Indeed the catalyst has to be

removed from the polymer by a water-quenching step that not only destroys the Lewis acid making reuse impossible but also leads to a large volume of acidic aluminum waste, unacceptable in these environmentally conscious days [9,10].

Therefore, the conversion of traditional homogeneous Lewis acid-catalyzed polymerization reactions into heterogeneous system represent a prime target in green chemistry and can offer many advantages: ease of separation, possible higher product yields and narrow molecular mass distribution due to pore-size distribution control, mild reaction conditions, less harm to the environment, catalyst reusability and less toxic effluent streams [11–13].

The immobilization of aluminum chloride on inorganic surface has been described in several articles and patents through the last three decades. Early work describes vapor deposition of AlCl$_3$ onto the support [14,15] before Drago et al. developed a method

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involving the use of a chlorinated solvent to solubilize anhydrous AlCl$_3$ before grafting [16,17]. The applications of this supported reagent have been largely restricted to Friedel–Crafts alkylations [18–20] or hydrocarbon cracking [21]. In 1995, Clark et al. [22] reported the preparation of supported aluminum chloride in toluene and subsequent work shows its activity in the production of hydrocarbon resins [23] and polymerization of aliphatic monomers [24].

We report here for the first time the use of supported aluminum chloride for the controlled polymerization of styrene. Apart from the advantage of easier reaction work-up, and recovery of the initiator the reaction is faster than in the homogeneous system and importantly control over the pore size of the support and external site doping can be used to give better control over polymer molecular weight.

## 2. Experimental

### 2.1. Reagents and instrumentation

The supports involved for the preparation of the catalyst were three mesoporous silica gels: Kieselgel K100 and K60 (surface areas of ca. 340 and 450 m$^2$ g$^{-1}$, respectively, from Merck) and Gasil AB725 (320 m$^2$ g$^{-1}$, from Crosfield Ltd.) and a non-porous material, Aerosil 200 (190 m$^2$ g$^{-1}$, from Degussa AG) and were dried at the required temperature before use. AlCl$_3$ was purchased from Aldrich (99.99%). Toluene (Fisher Chemicals) was dried over sodium metal. Styrene (99%, from Lancaster) was passed over an alumina column and dried over MgSO$_4$ overnight.

Nitrogen-adsorption studies were conducted on a Coulter SA3100. Prior to analysis, the samples were degassed at 110 °C for 3 h under vacuum. Diffuse reflectance infrared spectra (DRIFT) were obtained using a Bruker Equinox 55 FTIR spectrometer and a fast mercury–cadmium–telluride (MCT) detector. Solid samples were intimately grounded with KBr. $^{27}$Al MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz for $^1$H and $^1$H NMR were obtained on a Joel EX270 spectrometer operating at 270 MHz. Polymer molecular weights were measured by gel permeation chromatography (GPC) on a polymer laboratory chromatograph

equipped with two PL gel columns and calibrated over standard polystyrenes.

### 2.2. Preparation of supported aluminum chloride

A typical preparation of AlCl$_3$ catalyst was as follows. AlCl$_3$ (0.53 g, 4 mmol) was added to toluene (50 ml). The support material (5 g, calcined at 200 °C for minimum of 18 h) was added and the resulting slurry was stirred under a N$_2$ atmosphere at reflux temperature for 2.5 h. The solvent was removed under high vacuum at room temperature to obtain a yellow free flowing powder.

### 2.3. Infrared analysis

A small quantity of pyridine (ca. 5 ml) was placed at the bottom of an empty dessicator and samples tubes containing the catalysts were placed over it. The dessicator was then put under nitrogen atmosphere and sealed and the catalysts left overnight to adsorb the pyridine. Prior to DRIFT analysis, the samples were heated at 50 °C under vacuum for 30 min in order to remove the maximum of hydrogen-bonded pyridine.

### 2.4. Polymerization procedures

Polymerization reactions were carried out using styrene monomer and solid initiator (typically 0.41 mol% of active species) only under N$_2$ atmosphere. The styrene was outgassed with N$_2$ for 15 min prior to the addition of the supported aluminum chloride. The polymer solution was separated from the catalyst by filtration. Conversions were determined by $^1$H NMR and product molecular weights were measured by GPC in tetrahydrofuran.

## 3. Results and discussion

### 3.1. Solid acid structure

Nitrogen-adsorption studies indicate that treatment with AlCl$_3$ does not fundamentally alter the support structure. However, the reduction of both surface area and pore volume of the catalyst compared to the original silica material confirms the presence of Lewis acid moieties within the pores of the support. The
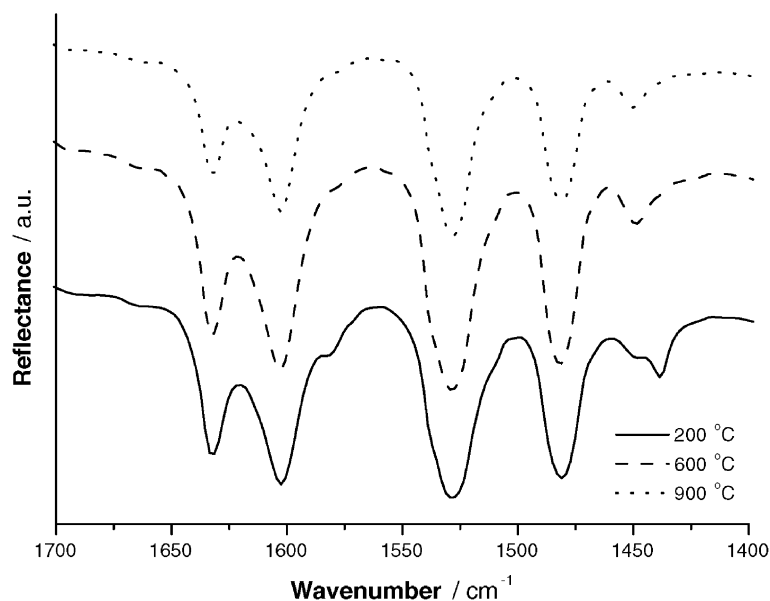
Fig. 1. DRIFT spectra of pyridine adsorbed on K100-OAlCl$_2$ with different silica pre-treatment temperatures.

nature of the active sites was examined by pyridine adsorption coupled with infrared spectroscopy [25]. The results were in accordance with previous finding by Drago et al., indicating the presence of both Lewis and Brønsted acidity on the surface (Fig. 1: bands at 1600 and 1448 cm$^{-1}$ assigned to Lewis bound pyridine, bands at 1635 and 1530 cm$^{-1}$ corresponding to the pyridinium ion, and band at 1480 attributed to either Lewis and Brønsted acidities) [26]. A typical $^{27}$Al MAS NMR spectrum for K100-OAlCl$_2$ is presented in Fig. 2. The peak at 2 ppm is due to the presence of 6-coordinate Al, formed when the catalyst is exposed to atmospheric moisture during the loading of the NMR tube. The peaks centered at 62 and 87 ppm were attributed to 4-coordinate Al with composition SiO-AlCl$_2$ and (SiO)$_2$-AlCl, respectively, both interacting with one hydroxyl group, whereas 5-coordinated species (SiO-AlCl$_2$ interacting with two SiOH groups) exhibit a peak at 35 ppm.

### 3.2. Homogeneous versus heterogeneous polymerization

Using equal amounts of anhydrous AlCl$_3$, faster reaction rates are observed when silica is involved in the polymerization reaction, either as the catalyst support or simply added to the reaction mixture with the homogeneous aluminum chloride (Fig. 3). Indeed, the rate of initiation, $R_i$, is nearly nine times greater for silica-OAlCl$_2$ catalyzed polymerization than for homogeneous AlCl$_3$ catalyzed polymerization. This could be explained by the presence of the silica surface silanol groups, acting as a proton donor co-catalyst, promoting faster initiation due to the close proximity of the different active sites. The heterogeneous catalyst presents therefore, a certain advantage over its homogeneous analogue, and can moreover be easily eliminated from the reaction mixture by filtration. Elemental analysis on the final polymer/monomer solution shows no significant traces of aluminum, indicating that the solid acid does not leach in the polymerization conditions used here. In contrast, the molecular weights of the polystyrene obtained with the heterogeneous catalyst are somewhat lower than those obtained with homogeneous aluminum chloride (Table 1). The rate of termination through transfer reaction, is increased by the presence of the silanol groups on the catalyst, which can act as terminating transfer agents, resulting in lower molecular weight polymers. Moreover, the polymer shows a bimodal distribution, suggesting a dual initiation mechanism, with different natures of acidic sites (Lewis or
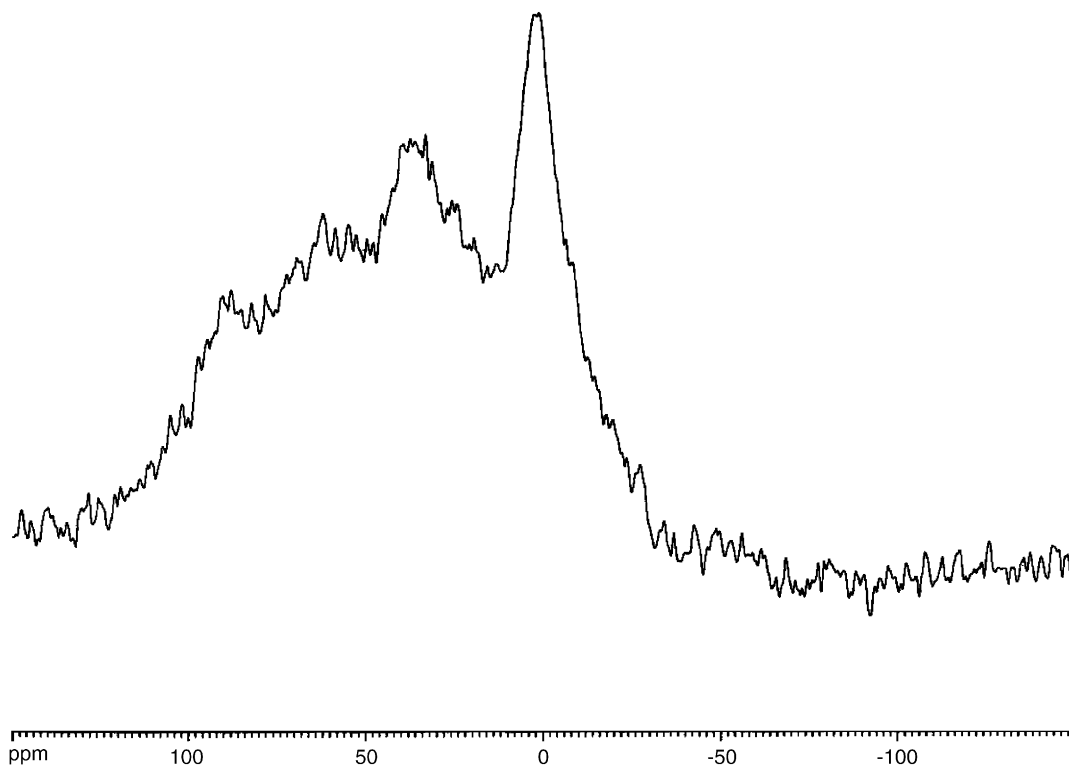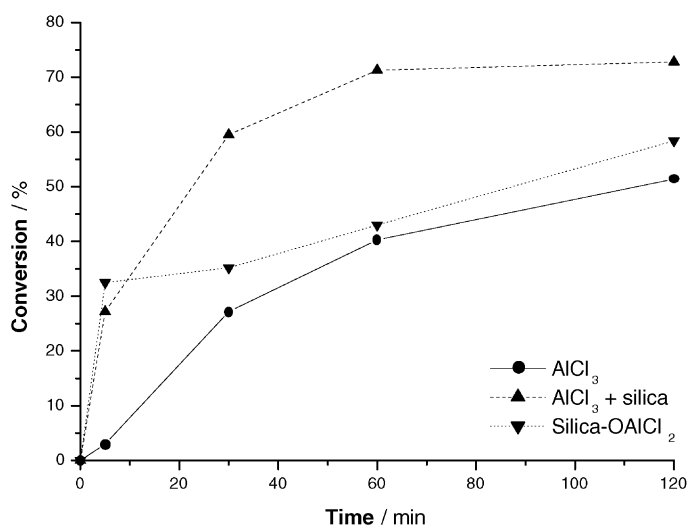
Fig. 2. $^{27}$Al MAS NMR spectrum of K100-OAlCl$_2$.

Fig. 3. Time–conversion curve for the polymerization of styrene with different catalysts.

Table 1
Homogeneous vs. heterogeneous polymerization of styrene with AlCl₃ catalysts[a]

| Catalyst | $M_n$ | $M_w/M_n$ |
|---|---|---|
| AlCl₃[b] | 2830 | 2.03 |
| AlCl₃ + K100 | 2390 | 2.43 |
| AlCl₂-K100[c] | 1480 | 2.56 |

[a] Polymerization carried out in bulk at 0 °C using [active species] = 0.41 mol%.

[b] Homogeneous catalyst

[c] Silica-OAlCl₂ catalyst with K100 as silica.

Brønsted) or the parallel propagation of two independent growing species with different initiating sites locations (in and out of the pores), leading to bimodal polymers with broader molecular weight distribution (higher polydispersity, $M_w/M_n$, when using silica).

### 3.3. Initiation process

Two hypotheses can be advanced to explain the bimodal polymer distribution.

First, since supported aluminum chloride possesses both Lewis and Brønsted acid sites on its surface [22]—the latter as a result of the silanol groups on the surface acting as weak Brønsted acid sites or as co-catalyst via activation by the Lewis acid moieties—

a dual initiation mechanism could be expected: direct Lewis acid initiation and catalyst/co-catalyst initiation with the interaction between the surface silanol groups and the Lewis moieties. A well-known proton scavenger, 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) [27], was used to ascertain whether or not direct initiation occurred. Fig. 4 shows that the polymerization virtually ceased at a ratio of $n_{DBMP}/n_{AlCl_3} = 0.44$. This behavior clearly indicates that no direct initiation takes place and that the initiation process occurs via a catalyst/co-catalyst system, the surface silanol groups and adventitious moisture acting as Brønsted moieties that activate the Lewis aluminum chloride species. Direct Brønsted initiation was eliminated as a possible mechanism due to the very low conversion obtained with the support on its own (less than 6%, whatever the pre-treatment temperature).

The bimodal polymer distribution is therefore attributed to the different location of the active species. Their presence on both the external surface and within the pores of the support is believed to promote the polymerization inside the catalysts' pores as well as on the external surface. The space limitation within the catalyst pores prevents the obtention of long polymer chains and thus might account for the lower molecular weight shoulder observed in the polymer GPC traces (Fig. 5), higher in intensity due to higher
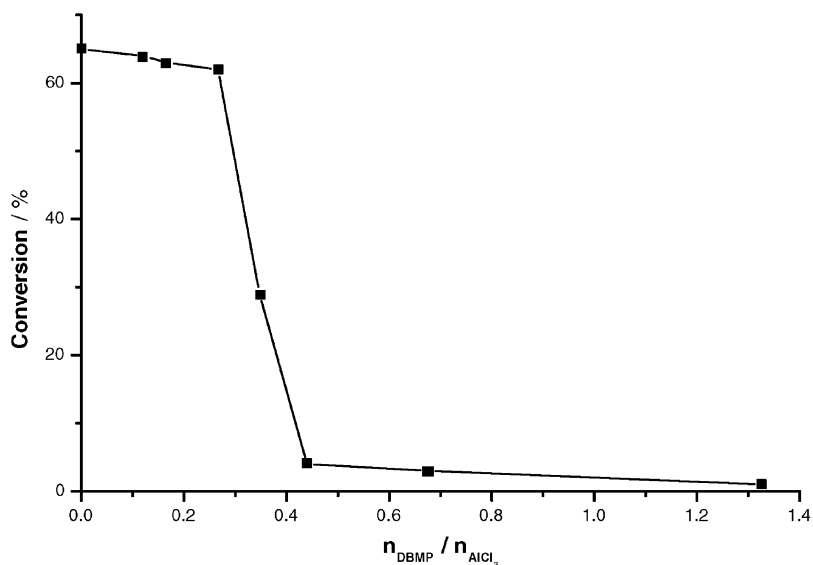


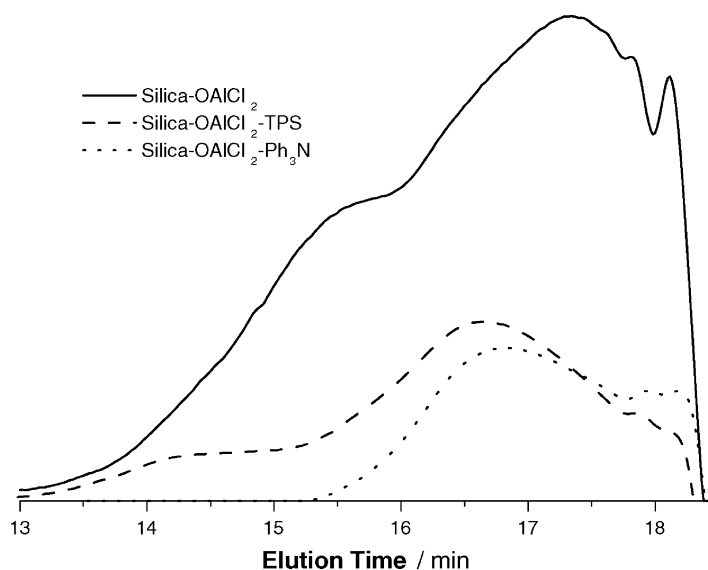Fig. 4. Effect of DBMP addition on the monomer conversion.

Fig. 5. GPC traces of the polystyrene products from reaction using silica-OAlCl$_2$ catalysts. Effect of catalyst modification. Polymerization carried out in bulk at 0 °C using [active species] = 0.41 mol%.

active sites concentration inside the pores. In order to test this and to improve molecular weight control, the effect of the external catalytic site blocker triphenylamine (Ph$_3$N post-treatment of the catalyst with AlCl$_3$:Ph$_3$N ratio 5:1) and of the external silanol groups' blocker triphenylchlorosilane (TPS-silica pre-treatment) on the solid acid was tested (Fig. 5) [28]. The presence of the bulky amine eliminates the higher molecular weight polymer consistent with the hypothesis. The elimination of some silanol groups by triphenylchlorosilane pre-treatment of the support shifts the polymer molecular weight towards higher molecular weight, as a possible result of the elimination of transfer reaction from the surface hydroxyl groups.

## 3.4. Influence of the catalyst support

Increasing the pore diameter of the silica support can increase the molecular weights of the polymer. For a mesoporous material, active sites are predominantly present inside the pore of the support. Therefore, space limitation inside the pore is a limiting factor for achieving high molecular weights. $M_z$, $z$—the average molecular weight, which is more sensitive than $M_w$ or $M_n$ to bigger polymer molecules, clearly in-

creases with the pore diameter of the support (Table 2). It can be noted that the activity of the catalyst is also lower for small pore supports (K60) but increases with an increase of the pore diameter of the support (K100 and Gasil). Rhodes and Brown [29] have suggested that for mesoporous materials, the total capacity of a support to adsorb active molecules corresponds to only ca. 20% of the total pore volume of the support. Bigger pores possess a higher concentration of active sites, increasing the overall activity of the catalyst. When using a non-porous material (e.g. Aerosil), where the

Table 2
Influence of catalyst support physical characteristic on polymerization of styrene with silica-OAlCl$_2$ catalysts[a]

| Catalyst support[b] | Pore diameter (nm) | Conversion[c] (%) | $M_z$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| K60 | 8.5 | 22 | 7050 | 1940 | 2.07 |
| K100 | 11.5 | 52 | 9000 | 1480 | 2.59 |
| Gasil | 13.9 | 46 | 11800 | 2260 | 2.56 |
| Aerosil | – | 100[d] | 16100 | 1980 | 3.36 |

[a] Polymerization carried out in bulk at 0 °C using [active species] = 0.41 mol%.
[b] Mesoporous materials except Aerosil, which is non-porous.
[c] Determined by $^1$H NMR after 2 h.
[d] Obtained after ca. 5 min.

pore size is virtual, both activity and molecular weight ($M_z$) are enhanced compared to mesoporous materials. Fast and complete polymerization is obtained using the Aerosil supported catalyst due to the increased accessibility of the monomer molecules to the active sites, all present on the external surface of the material.

### 3.5. Support hydration level

The grafting of the active species onto the support surface occurs via bond formation between surface silanol groups and the Lewis acid. The nature and concentration of the silanol groups on the silica gel is highly temperature dependent. Drago et al. [26] have outlined the importance of the silica hydration level in the synthesis of the supported aluminum chloride catalyst, showing that insufficiently dried support material contributes to the hydrolysis of aluminum chloride, giving an inactive catalyst. Product molecular weights can be increased by using a silica support pre-treated at higher temperatures (Table 3); indeed the supported reagent prepared using 900 °C calcined silica shows a dramatic shift in the product GPC trace towards higher molecular weight products (Fig. 6). When pre-treated at 200 °C, physisorbed wa-

Table 3
Influence of K100 pre-treatment temperature on cationic polymerization of styrene by AlCl2-K100 catalysts

| K100 pre-treatment temperature (°C) | Conversion (%) | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| 25 | 0 | – | – |
| 100 | 28 | 1950 | 2.76 |
| 200 | 52 | 1480 | 2.56 |
| 400 | 44 | 1940 | 2.43 |
| 600 | 60 | 2120 | 2.50 |
| 900 | 42 | 2390 | 2.54 |

ter is removed from the silica surface leading mainly to hydrogen-bonded silanol groups (vicinal) [30] whereas at 600 °C isolated silanols are the dominant species, in reduced concentration. Further calcination condensed the silanols leading to the formation of more strained and reactive siloxane bridges. From the pyridine titration of the catalyst (Fig. 1), it can be noticed that the very weak band observed at 1448 cm$^{-1}$ for the catalyst pre-treated at 200 °C corresponding to coordinatively bound pyridine is very slightly shifted towards higher wavenumber (1450 cm$^{-1}$) for higher pre-treatment temperature (600 and 900 °C), suggesting a small increase in the interaction strength. A
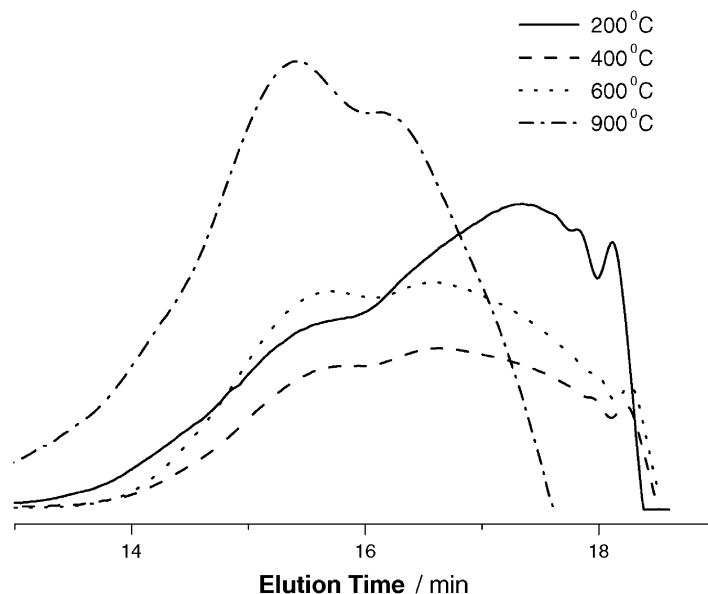


Fig. 6. GPC traces of the polystyrene products from reaction using silica-OAlCl2 catalysts. Effect of pre-calcination temperature of the silica support. Polymerization carried out in bulk at 0 °C using [active species] = 0.41 mol%.
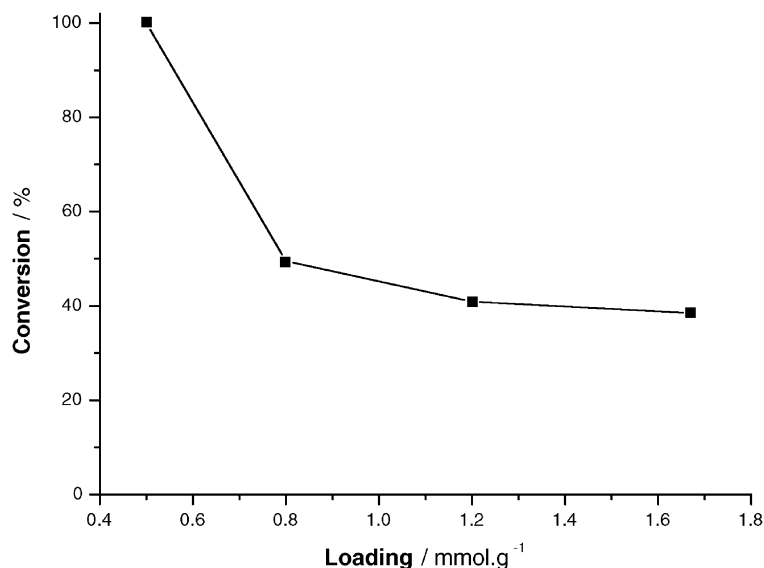
Fig. 7. Effect of Al loading on the styrene polymerization using silica-OAlCl$_2$ catalysts. Polymerization carried out in bulk at 0 °C using [active species] = 0.41 mol%.

more efficient grafting of the active species obtained at lower silanol group concentration (reaction with isolated silanols), leading to possibly stronger active sites, in conjunction with the reduction of polymer chain termination due to proton transfer between the surface silanol groups and the cationic polymer chain, leads to higher molecular weight polymers. The partial collapsing of the smallest silica pores at high temperature can also reduce the formation of small polymer chains. At very high calcination temperatures such as 900 °C, the elimination of all the silanol groups decreases the formation of the initiating Lewis/Brønsted acids catalyst/co-catalyst complex, thus reducing the activity of the catalyst as the moisture present in the reaction mixture (e.g. from the monomer) correspond to the only source of proton. For the molecular weight distribution at this pre-treatment temperature, it is interesting to contrast the result with those from the support modification shown earlier (Fig. 5): very high calcination temperatures cause the opposite effect to Ph$_3$N. At 900 °C, the partial collapse of the silica framework structure witnessed by a large reduction in surface area and pore volume (surface area drops from 333 to 171 m$^2$ g$^{-1}$ and pore volume from 0.939 to 0.592 cm$^3$ g$^{-1}$ at 600 and 900 °C, respectively) causes the active sites to be essentially external to

the pores of the catalyst. This is confirmed by the effect of this catalyst on the polymer molecular weight distribution, as the GPC trace shown in Fig. 6 is similar if somewhat narrower—owing to a decrease in surface silanol groups concentration, promoting less transfer reactions—to that obtained from non-porous Aerosil supported catalyst.

### 3.6. Active species loading

At identical [active sites]/[monomer] ratio, the loading of aluminum centers on the silica support also has a large effect on the rate of polymerization. As shown in Fig. 7, a drop in monomer conversion at high AlCl$_3$ loading is observed. Investigations by Hu et al. [31] have shown that AlCl$_3$ loading on a silica surface is limited by the concentration of surface silanol groups. Above a maximum loading of about 1.9–2 mmol g$^{-1}$, free AlCl$_3$ could be found on the catalyst surface [32], leading to homogeneous reaction, and thus leaching of the catalyst in the polymer solution. Interestingly, the fastest rates of polymerization are achieved at lower Al loading; this can be attributed to the need for available surface OH groups providing the necessary Brønsted acidity (via coordination to neighboring Al centers) for fast reactions. The very fast reactions observed at low

Al loading lead to very low molecular weight products whereas no drastic changes in the molecular weight ($M_n$) were observed for the polymers using catalyst at higher loading.

These results show how the variables available in the design of a solid acid (access to pores and pore size, activation temperature, loading, etc.) can be used to control the molecular weight of products from polymerization reactions initiated by surface sites.

### 3.7. Polymerization extension

Preliminary solid acid reuse experiments have been carried out. Once a batch polymerization was complete, additional styrene was added, leading to further, if slower polymerization. Active moieties are therefore still present in the reaction mixture, either as initiating or growing species. The molecular weight was increased during the second batch polymerization ($M_{n1} = 1980$ and $M_{n2} = 3090$) whereas the polydispersity decreased, indicating the growth of the existing polymer chains. Few new polymer chains were formed, due to a possible blockage of the active sites or the pores by the existing chains, limiting the diffusion of new monomer molecules to the active moieties. Indeed, the analysis of the catalyst after use by IR spectroscopy (DRIFT) and thermal analysis showed the presence of polystyrene. Moreover, the surface area of the catalyst after use is significantly reduced (from 300 to 200–250 $m^2 g^{-1}$). These results demonstrate the possibility of the use of AlCl$_2$-silica catalyst in a partially continuous process in a controlled atmosphere, or its reuse. Work aimed at eliminating polymer retention on the catalyst surface and regenerating the proton sources is currently under investigation.

### 4. Conclusion

In conclusion, we have shown that solid acids based on aluminum chloride, chemisorbed on silica are active and stable catalysts for the polymerization of styrene. Their use simplifies the polymer isolation process and eliminates an aqueous containing waste stream. The initiation process occurs according to a catalyst/co-catalyst mechanism, with the surface hydroxyl groups providing the most important source of proton. The molecular weight of the polymer is greatly influenced by the concentration of the silanol groups on the surface of the silica. For high OH concentration, obtained by low catalyst loading or low calcinations temperature, low molecular weights are obtained, leading us to believe that these surface hydroxyl group can act as proton transfer agents. High initiation rate and predominant rate of chain termination by transfer reaction over propagation rate are a result of high silanol group concentration. The pore structure and sites distribution in the solid acids can be adjusted so as to control the molecular weight distribution of the polymer product.

### Acknowledgements

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