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# Supported copper triflate as catalyst for the cationic polymerization of styrene

Valérie Sage, James H. Clark [*], Duncan J. Macquarrie

*Green Chemistry Group, Clean Technology Centre, University of York, Heslington, York, YO10 5DD, UK*

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**Abstract**

Silica-supported copper triflate catalysts have been prepared and used in the heterogeneous cationic polymerization of styrene in an attempt to reduce the environmental hazards associated with the traditional vinyl polymerization catalyzed by homogeneous Lewis acid. Faster reactions and higher molecular weight polymers were observed compared to the homogeneous catalyst. However, the presence of active sites both within the pores and on the external surface, and the possible availability of different types of catalytic sites, leads to broad polymer molecular weight distribution. The catalysts exhibited both Lewis and Brønsted acidities due to the presence of residual moisture within $Cu(OTf)_2$, as well as the surface silanol groups of the silica and the methanol used as solvent in the catalyst preparation. Initiation occurs via a catalyst/cocatalyst process and water has proven to play a major role as the cocatalyst. Proton transfers from the growing polymer molecules to the initiating species or to the monomer represent the principal termination mechanism. The reuse of the catalyst was limited by the blocking of the pores by the polymer chains, reducing the diffusion of the monomer units to the active sites.

*Keywords:* Cationic polymerization; Silica; Acid catalyst; Copper triflate; Green Chemistry

## 1. Introduction

Homogeneous Lewis acids represent the most commonly used catalysts for the fast and efficient cationic polymerization of vinyl monomers in research studies (e.g., $AlCl_3$ [1], $BF_3$ [2]). However the reaction processes are highly exothermic, often using large volumes of chlorinated solvents, and control over the molecular weight of the polymer is generally poor. In addition, the separation of the Lewis acid from the reaction products produces a large volume of acidic waste due to the water-quenching step needed to neutralize the acid. New environmental legislation calls for reduction of waste production and the use of more environmentally friendly alternative solvents and catalysts, which makes the current homogeneous polymerization system environmentally unacceptable [3].

The substitution of traditional homogeneous Lewis and Brønsted acid catalysts for heterogeneous ones, e.g., solid acid catalysts, could constitute a more environmentally friendly alternative to the polymerization process. Such catalysts offer many advantages compared to their homogeneous counterparts: milder reaction conditions, no need for solvents or the use of less toxic ones (e.g., hydrocarbons), easier separation of the catalyst from the reaction mixture by filtration, and its possible regeneration and reuse, reducing the production of waste (no water-quenching step) and thus harm to the environment. A few examples exist of such processes—for example, Aida and co-workers have used mesoporous Al–Si MCM-41 to carry out highly controlled polymerization of lactones using the pore system to hinder transesterification reactions, thus obtaining excellent control over molecular weight distribution [4]. Spange et al. have also published on mesoporous silica-supported carbocation-based systems for polymerization of carbazoles and vinyl ethers [5].

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[*] Corresponding author. Fax: +44 1904 434546.
*E-mail address:* jhc1@york.ac.uk (J.H. Clark).

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In a previous paper, the use of silica-supported aluminum chloride as catalyst in the cationic polymerization of styrene was reported [6]. Although this catalyst presents some indubitable advantages over the generally used homogeneous catalysts, its extreme sensitivity to air and moisture limits its application, and it must be handled under an inert atmosphere. Another Lewis acid, copper trifluoromethanesulfonate (copper triflate, $Cu(OTf)_2$), a less sensitive Lewis acid, was therefore considered. Metal trifluoromethanesulfonates or triflates (OTf) present the advantages of being water tolerant and less sensitive toward atmospheric exposure than halide Lewis acids. Moreover, their efficiency in cationic polymerization of vinyl monomers in aqueous media was previously demonstrated (using $Al(OTf)_3$ [7,8], $Yb(OTf)_3$ [9,10], and $Cu(OTf)_2$ [11]).

A few examples of supported Cu species for use in atom transfer radical polymerization have been reported. Matyjaszewski and co-workers demonstrated the use of a silica–polyamine material, which coordinated Cu and was used in the polymerization of styrene, methyl acrylate, and methyl methacrylate [12]. Good activity and reusability were demonstrated and losses of Cu were low. A related system was disclosed by Zhu and co-workers [13], which involved the physisorption of a Cu–polyamine complex onto silica, and its use in the polymerization of methyl methacrylate. In this case good activity and reasonable recyclability were demonstrated, although no specific data on Cu loss were provided. While the relatively basic environment afforded by the amine ligands precludes acid-catalyzed polymerization in these examples, making the polymerization mechanistically different, both papers describe active and recyclable polymerization catalysts.

A few examples of triflate compounds immobilized onto solid supports have been described in the literature. For instance, $Sc(OTf)_3$ immobilized on polymer (Nafion NR-50) catalyzed the alkylations of carbonyl compounds [14], $Zn(OTf)_2$–silica was used for $\alpha$-pinene oxide rearrangement [15], and solvent-free thioacetalization of carbonyl compounds were catalyzed by $Cu(OTf)_2$–silica [16]. It is therefore believed that the present application of silica-supported copper triflate as catalyst for the cationic polymerization of styrene is unprecedented in the literature.

## 2. Experimental

### 2.1. Reagents and Instrumentation

Kieselgel K100 was used as support for the preparation of the heterogeneous catalysts (surface area of ca. 340 $m^2\,g^{-1}$, from Merck) and was dried at the required temperature before use. $Cu(OTf)_2$ was purchased from Lancaster (98%) and contains a nonnegligible amount of moisture. Toluene (Fisher Chemicals) was dried over sodium metal. Styrene (99%, from Lancaster) was passed over an alumina column and dried over $MgSO_4$ overnight.

$N_2$-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 using a fast mercury–cadmium–telluride (MCT) detector. Solid samples were intimately ground with KBr. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed simultaneously on a Stanton Redcroft STA 625 instrument. Between 10 and 20 mg of sample were analyzed at a time under a constant flow of nitrogen gas, at a heating rate of 20 K/min. Neutral alumina was used as the reference material for the DTA analysis, and the instrument was calibrated regularly using copper sulfate pentahydrate. $^1H$ and $^{19}F$ solution-state NMR spectra were recorded on a Joel EX270 spectrometer (operating at 270 MHz for $^1H$), with a probe temperature of 30 °C. $^{19}F$ MAS NMR spectra of the silica-supported catalysts were recorded by Dr. Stewart J. Tavener, from the Green Chemistry Group, University of York, on a Bruker Avance 400 spectrometer operating at 400 MHz for $^1H$. The samples were inclined at an angle of 54.7° to the magnetic field and the magic-angle rotor-spinning rate was typically 25 kHz (2.5 mm rotor). Atomic absorption spectroscopy (AAS) measurements were obtained on a Philips Ph9200 atomic absorption spectrophotometer. The $Cu(OTf)_2$-supported catalyst (approximately 60 mg) was dissolved in $HNO_3$ concd (5 ml) overnight, then diluted with $H_2O$ in a volumetric flask (50 ml), and measured against copper standard solutions. For testing the leaching of the catalyst in polymerization reaction, the polymer (60 mg) was dissolved in THF and diluted with $H_2O$ in a volumetric flask (50 ml). Gel-permeation chromatography of the polymers were performed by Dr. Kamelia V. K. Boodhoo, from the Process Intensification & Innovation Centre (PIIC), University of Newcastle Upon Tyne, on a Polymer Laboratories chromatograph fitted with two columns (PLgel 5-µm Mixed-C columns with 5-µm PLgel guard) maintained at 30 °C throughout the measurement. The instrument was calibrated with polystyrene standards (high and low molecular weights) and THF was used as solvent at a flow rate of 1 $ml\,min^{-1}$.

### 2.2. Preparation of supported copper triflate

A typical preparation of $Cu(OTf)_2$ catalyst was as follows. Copper trifluoromethanesulfonate (0.18 g, 0.5 mmol) was added to methanol (50 ml) in a 100-ml 3-neck round-bottom flask equipped with a reflux condenser and a magnetic stirrer bar. The support material (5 g, pretreated at 600 °C for 18 h) was added and the resulting slurry was stirred at room temperature under $N_2$ atmosphere for 2.5 h. The solvent was then evaporated in vacuo at 80 °C for 1 h. The resulting solid product obtained was white or light blue depending on the loading.

### *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 0.115 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 copper triflate catalyst. 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.

### *2.5. Polymerization with 2,6-di-tert-butyl-4-methylpyridine (DBMP)*

The polymerization procedure was the same as the one described in Section 2.4, except that various amounts of DBMP were added to the $Cu(OTf)_2$–silica catalyst in toluene (10 ml, Na dried) and stirred for 30 min under $N_2$ prior to the addition of styrene (5 ml, 43.46 mmol).

## 3. Results and discussion

### *3.1. Catalyst characterization*

The grafting of copper triflate onto the silica occurs mainly within the pores of the mesoporous support, as demonstrated by the drop in both surface areas and pore volumes obtained by nitrogen-adsorption studies (Table 1). However, all the nitrogen adsorption isotherms and pore-size distribution curves of various $Cu(OTf)_2$-supported catalysts are similar in shape to those of the parent silica (Fig. 1), indicating that the grafting did not significantly alter the physical structure of the parent silica and the resulting catalyst is stable up to 380 °C, before the Lewis acid decomposes to copper fluoride (STA studies).

STA studies were used to confirm the presence of triflate groups on the catalyst. The curves presented in Fig. 2 represents a typical STA graph of a K100 supported $Cu(OTf)_2$ (0.1 mmol $g^{-1}$ loading). The endotherm centered at 55 °C, accompanied by a weight loss of around 1%, corresponds to the loss of water and/or solvent (methanol). The other important event is the exothermic decomposition of the triflate groups between 330 and 400 °C (centered at 376 °C, from the derivative of the weight loss). The decomposition

Table 1
Physical parameters of several silica-supported copper triflate catalysts (support pretreated at 600 °C)

| Catalyst | Physical parameters | | |
|---|---|---|---|
| | BET surface area ($m_2$ $g^{-1}$) | Pore volume ($cm^3$ $g^{-1}$) | Pore diameter[c] (nm) |
| $Cu(OTf)_2$-K100[a] | 280 | 0.880 | 8.74 |
| K100[b] | 330 | 0.939 | 8.83 |

[a] Catalyst prepared at 22 °C with a support pretreated at 600 °C; 0.1 mmol $g^{-1}$.

[b] Pretreated at 600 °C.

[c] BJH desorption average pore diameter.

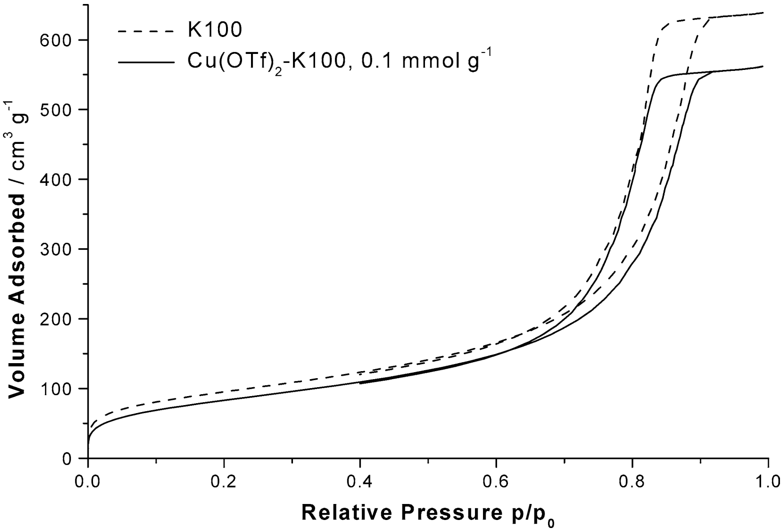

Fig. 1. Typical nitrogen adsorption isotherm of silica K100 and $Cu(OTf)_2$ supported on K100. All supports were pretreated at 600 °C.

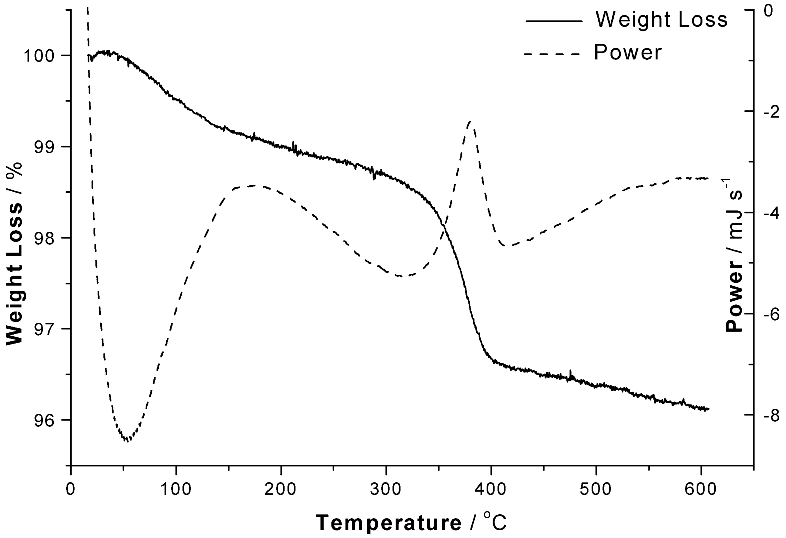

Fig. 2. STA traces of $Cu(OTf)_2$ on silica (0.1 mmol $g^{-1}$).

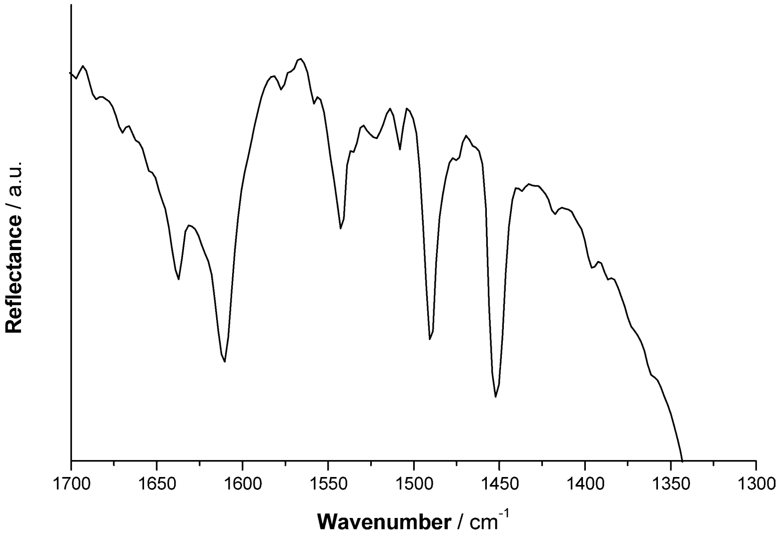

Fig. 3. DRIFT spectra of silica-supported $Cu(OTf)_2$ after pyridine adsorption.

of supported copper triflate occurs at a lower temperature than for pure copper triflate (376 and 415 °C, respectively). The same reduction in thermal stability was observed for silica-supported lanthanide chlorides [17] and zinc triflate [15] when compared to the pure salt. In the second case, this was ascribed to the reaction of highly dispersed Lewis acid with silica surface silanol groups, hydrolyzing the Zn–(OTf) bond to form ZnO and triflic acid. The authors ruled out the possibility of weight loss being caused by the loss of physisorbed triflic acid formed during the catalyst preparation and concluded that it reflected the thermal decomposition of the triflate groups. A similar process is expected to occur with silica-supported $Cu(OTf)_2$.

Pyridine adsorption coupled with infrared spectroscopy was used to determine the nature of the active site of the supported copper triflate catalyst [18]. The results indicate that the catalysts present both Lewis and Brønsted acid sites, which might both contribute to the catalytic activity of the materials in the cationic polymerization (Fig. 3; two intense peaks at 1450 and 1610 $cm^{-1}$, together with a weaker one at 1580 $cm^{-1}$, assigned to the presence of Lewis acid sites [15], two bands at 1540 and 1637 $cm^{-1}$ corresponding to the Brønsted acidity (pyridinium ion) and the remaining band at 1490 $cm^{-1}$ ascribed to pyridine bound at either a Lewis or a Brønsted acid site). The presence of Brønsted acidity on the supported catalyst can result from the interaction of the triflate groups with the silica silanol groups and the water present in the system.

### 3.2. Homogeneous versus heterogeneous polymerization

The heterogeneous catalyst must offer better performance than the homogeneous one to overcome the extra cost of the catalyst preparation. The reaction rates for the copper

Table 2
Homogeneous vs heterogeneous polymerization of styrene with $Cu(OTf)_2$ catalysts[a]

| Polymerization catalyst | Time for 100% conversion (min) | $M_z$ | $M_w$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| $Cu(OTf)_2$ | 8 | 2690 | 980 | 460 | 2.13 |
| $Cu(OTf)_2$-K100 | 3 | 9490 | 2260 | 510 | 4.43 |

[a] Polymerization carried out in bulk at 22 °C with 43.56 mmol styrene; $[Cu(OTf)_2]_0 = 0.115$ mol% (0.1 mmol $g^{-1}$, pretreated at 600 °C).

triflate-catalyzed polymerizations are very fast as the reactions with either the homogeneous or the heterogeneous $Cu(OTf)_2$ catalysts were complete (100% conversion) within a few minutes at very low catalyst concentration (Table 2). However, the supported catalyst enhances the overall polymerization rate as the reaction reaches completion in a shorter period of time (no exact reaction rates values were calculated). In addition, higher molecular weight polymers are observed with the heterogeneous catalyst. A larger proportion of very high molecular weight polymer chains are obtained with the supported catalyst (higher $M_z$), although their amount is smaller as $M_n$ is nearly the same. The low values of $M_n$ suggest a predominance of the initiation rate over the propagation and transfer/termination ones. Previous studies on cationic polymerizations catalyzed by metal triflate suggest that the initiation occurs according to a cocatalysis mechanism with the water present in the system [8,9]. Indeed, homogeneous polymerization performed with dried $Cu(OTf)_2$ as catalyst (dried under vacuum for 3 h at 100 °C prior reaction) was much slower than when hydrated homogeneous copper triflate was used. While 100% conversion was achieved in 8 min with the latter, 20 min was needed to complete the reaction with the dried catalyst. This confirms the importance of water in the polymerization system as reduction in its concentration decreases the polymerization rates. The water present in the system originates from the traces of moisture present on the catalyst, in the monomer, and on the walls of the reaction vessel.

In addition to the water molecules, the surface silanol groups of the support are also expected to play a cocatalytic role in the polymerization process (Brønsted acidity), hence the faster conversion observed for the silica-supported $Cu(OTf)_2$.

The polymer molecular weight distribution was, however, broader when obtained with the silica-supported copper triflate catalyst than with the homogeneous Lewis acid, and a multimodal polymer weight distribution was obtained. It is believed than when porous materials are used as the catalyst supports, active sites within and out of the pores will behave differently, contributing to the broader molecular weight distribution. A high molecular weight polymer can be expected to be obtained due to external active site initiation, whereas a lower molecular weight one is expected from the in-pore polymerization, as a result of the pore-size restriction. Constraints on polymer structure and molecular weight have been seen previously, and have been ascribed to pore effects [4,5a,19]. However, the complexity of the molecular weight distribution may indicate that this picture is oversimplified, and that several types of site, each with different activity, exist.

It is possible that the slower conversion and lower molecular weight obtained with the homogeneous Lewis acid are caused by an increase of the termination reaction, as well as by a slower initiation or propagation. The low polymer molecular weight and the very fast monomer conversion obtained with the heterogeneous catalyst suggest a very fast initiation, occurring both on the external surface and within the pores of the catalyst. This rapidly consumes all the monomer available, hence preventing the formation of long polymer chains. Moreover, a high initiation rate may also be a result of an increased rate of transfer reaction. As previously reported for polymerization using silica-supported catalyst [6], the silanol groups present on the surface of the $Cu(OTf)_2$–silica catalyst might play the dual role of cocatalyst (together with the adventitious water and methanol arising from the surface) and transfer agents, hence the fast conversion and high polydispersity obtained.

Liquid $^{19}F$ NMR analyses of the final polymer were performed to investigate the leaching of the catalyst during polymerization or its stability toward hydrolysis to form triflic acid. With a 0.1 mmol $g^{-1}$ $Cu(OTf)_2$–silica catalyst, no triflic acid ($\delta_{\text{triflic acid}} = -78.5$ ppm) or triflate groups could be detected. $Cu(OTf)_2$–silica does therefore not form significant amounts of triflic acid or substantially lose triflate groups under the experimental conditions. AAS was used in addition to $^{19}F$ NMR to measure the level of copper in the monomer/polymer mixture after elimination of the catalyst. With an optimum loading (up to 0.15 mmol $g^{-1}$), the supported catalyst does not leach substantially during the course of the reaction, independently of the hydration level of the support. Indeed, with a catalyst loading of 0.1 mmol $g^{-1}$ of copper triflate, no copper was detected in the final polymer (a detection limit of 2% was evaluated for AAS, similar to that obtained with elemental analysis on the spent catalyst) and the contribution of homogeneous species to the polymerization process should be small. However, given the rapidity of the polymerization, and the large increases in viscosity accompanying the polymerization, a filtration test—to test the activity of the monomer/polymer mixture once the catalyst was removed, i.e., possible homogeneous active sites—was not practicable.

## *3.3. Mechanistic investigations*

### *3.3.1. Nature of the catalyst active sites*

Two cationic initiation mechanisms are theoretically possible in the polymerization process catalyzed by silica-supported copper triflate: direct initiation by the Lewis acid sites or cocatalyst initiation with the Brønsted acid sites (originating from residual moisture or possibly from the silanol groups). Investigations of the initiation mechanism were performed in the presence of the proton trap 2,6-di-

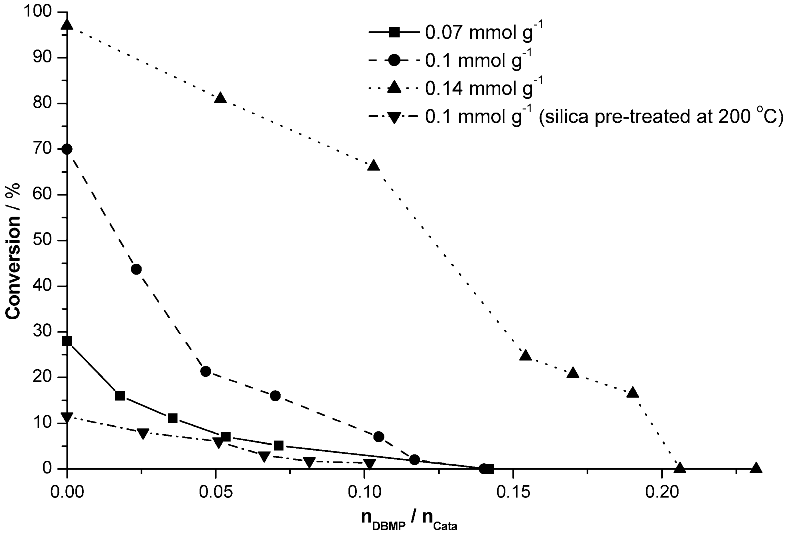

Fig. 4. Effect of DBMP concentration on styrene polymerization (in toluene) using $Cu(OTf)_2$-K100 catalyst at different loadings, ($Cu(OTf)_2 = 0.05$ mmol, support pretreated at 600 °C).

*tert*-butyl-4-methylpyridine [20]. This hindered pyridine selectively inhibits all the Brønsted acid sites, leaving only the Lewis acid moieties as potential initiating sites via direct initiation—if this takes place. Different loadings and pretreatment temperatures were investigated, and the conversion results of the polymerization using different initial DBMP concentrations for a constant amount of $Cu(OTf)_2$ (0.05 mmol) are presented in Fig. 4. The catalyst was mixed with DBMP in toluene (10 ml) for 1/5 hour prior to the addition of the monomer, to allow sufficient time for all the DBMP to coordinate with any protic sites.

For all the catalysts tested, the monomer conversion decreases gradually with higher concentration of DBMP, until polymerization ceased. The total inhibition of the polymerization with critical amount of DBMP confirms that the initiation step only takes place in the presence of protic moieties according to a cocatalyst mechanism with Lewis and Brønsted species. No other initiation mechanism occurs; i.e., direct Lewis initiation, and the multimodal distribution of the polymer is, at least in part, due to the presence of different active sites, including those in and out of the support pores.

The Brønsted acid sites involved in the initiation process represent only a small fraction of the active sites of the catalyst, and are different for each catalyst loading and pretreatment temperature. For example, for a supported catalyst loaded with 0.1 mmol $g^{-1}$ of copper triflate and pretreated at 600 °C, only around 13% of the total acid concentration corresponds to the Brønsted acid sites ($n_{DBMP}/n_{Cu(OTf)_2} = 0.13$ for complete polymerization inhibition), assuming that all the Brønsted species arise from the surface of the catalyst. These sites are therefore very active, as complete conversion can be obtained for bulk polymerization.

Four types of protic species are present in the polymerization system catalyzed by $Cu(OTf)_2$–silica and capable of cocatalyst behavior: the adventitious moisture from the monomer and reaction vessel, the remaining hydration water of pure copper triflate, the methanol on the catalyst surface resulting from the grafting process, and the surface silanol groups of the silica. However, although not measured, the concentration of adventitious moisture arising from the monomer and the reaction vessel remains constant for polymerizations performed using the different catalysts and can therefore not account for the difference in the Brønsted acid site concentrations obtained for each catalyst, as each polymerization reaction was reproducible within a 3% error margin. Increasing the loading of $Cu(OTf)_2$ on the surface of the catalyst increases the amount of water arising from the hydration level of $Cu(OTf)_2$, while the concentration of silanol groups slightly decreases. As the proportion of Brønsted active sites increases with increasing loadings of $Cu(OTf)_2$ (11, 13, and 21% for 0.07, 0.1, and 0.14 mmol $g^{-1}$ loading, respectively), it can be deduced that the hydration water of the Lewis acid is mainly responsible for the Brønsted active sites initiating the polymerization. The higher conversions obtained at higher catalyst loadings are therefore due to an increased amount of initiating sites.

With a support pretreated at 200 °C, the total number of silanol groups on the catalyst surface is larger than at 600 °C; thus, it is expected that a higher concentration of Brønsted sites should be observed. However, a lower proportion of Brønsted active sites is observed if the support is pretreated at 200 °C (10% of the total acid concentration, as $n_{DBMP}/n_{Cu(OTf)_2} = 0.1$ for complete polymerization inhibition, compared to 21% at 600 °C), which might suggest that only certain types of silanol groups are active for polymerization. We might speculate that those are isolated or on the edge of the H-bonded regions. The concentration of silanol groups has therefore a major effect on the activity of the catalyst. At higher concentrations, i.e., at lower loading or pretreatment temperature, they reduce the activity of the catalyst, possibly through higher transfer/termination rates (see Section 3.3.3). The next section analyses more closely the

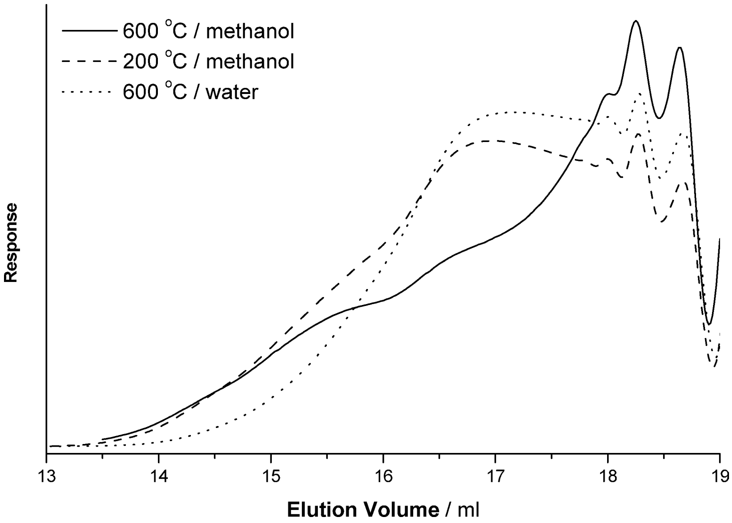

Fig. 5. Polystyrene GPC traces obtained with $Cu(OTf)_2$-K100 catalyst (pretreatment temperature/preparation solvent).

influence of the different protic species on the polymerization mechanism.

### 3.3.2. *Contribution of the protic species*

Under the standard polymerization conditions (support pretreated at 600 °C and catalyst prepared in methanol at room temperature, with a loading of 0.1 $mmol\,g^{-1}$), initiation is predominant over propagation and complete conversion is obtained in 3 min. If the support pretreatment temperature prior to the grafting of copper triflate is lowered to 200 °C, slower conversion is observed (complete conversion in 30 min), without drastic changes in the molecular weight ($M_n = 620$ and $M_w/M_n = 4$, as opposed to 510 and 4.43, respectively, for standard conditions). As indicated in the previous section, such a catalyst has fewer Brønsted active sites (around 10%) than when pretreated at 600 °C (13%). In addition, the weight distribution profile of the polymer obtained with this catalyst shows a large increase of the low molecular weight shoulder (Fig. 5), which might indicate a higher rate of transfer/termination reaction. The same behavior in terms of conversion, molecular weight, and its distribution is observed for polymers obtained with a catalyst prepared in water, where partial rehydration of the surface can occur. Silanol groups therefore act as transfer agents. However, their action can be considered as a terminating process as the resulting cation ($–Si–OH_2^+$) is inactive in initiating further polymerization. For high silanol group concentration, their potential as transfer/terminating agents might therefore predominate over their possible cocatalyst effect. Although it has been demonstrated in the literature that the weakly acidic surface silanol groups could add to a vinyl double bond forming a carbocation intermediate, promoting a direct Brønsted initiation mechanism [21], the extent to which this occurs remains quite small, as demonstrated by the low conversion obtained with only silica as catalyst (pretreated at 200 °C, 5% conversion).

The reduction of the hydration level and methanol content of the copper triflate catalyst by extended drying prior to polymerization also decreases the polymerization rate (100% conversion achieved in 60 min as opposed to 3 min for the control polymerization). A higher molecular weight polymer with similar polydispersity is then obtained ($M_n =$ 1030 and 510, $M_w/M_n = 4.1$ and 4.43, for polymerization with the dried catalyst and under standard conditions, respectively). This indicates that fewer initiations take place. Based on the theoretical molecular weight, the molecular weight is expected to be higher if the concentration of initiating species decreases. The loss of activity for the dried catalyst confirms the essential contribution of the water of hydration in the polymerization process as a cocatalyst during the initiation.

### 3.3.3. *Initiation and termination mechanisms*

The previous experiments demonstrated that supported copper triflate induces the polymerization of styrene in the presence of water (adventitious moisture or hydration water) or methanol (physisorbed on the catalyst surface) according to a cocatalyst mechanism. An initiation mechanism considering the copper triflate hydration molecules as cocatalyst is illustrated in Fig. 6. No direct Lewis initiation is occurring as the polymerization can be completely inhibited in the presence of a proton trap. The mechanism is similar to that suggested in the literature for other cationic polymerizations catalyzed by metal triflate [7,8].

Furthermore, the reduction in the initiation rate observed with a highly dried catalyst suggests that the water/moisture is probably consumed during the polymerization process preventing further cocatalyst action. It has been previously reported for the polymerization of styrene by a metal triflate that the hydroxyl anion can be incorporated in the propagating chain to terminate the polymer as shown in Fig. 7 [9]. The same phenomenon could happen with supported copper triflate, progressively reducing the concentration of water

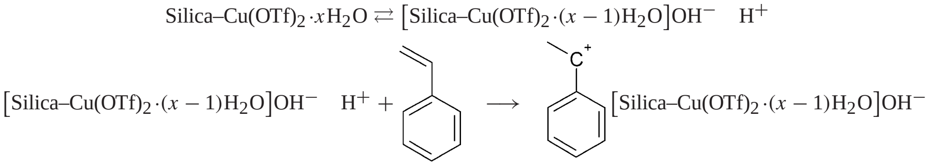

Fig. 6. Initiation of styrene polymerization by supported copper triflate.

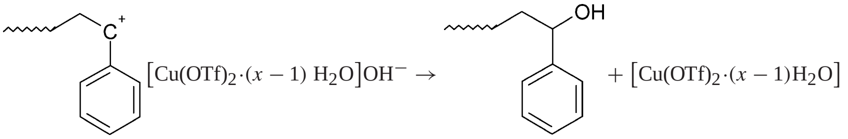

Fig. 7. Termination reaction with the hydroxyl anion.

through the reaction. This mechanism decreases the initiation rate, hence the slower conversion and the higher molecular weight polymer distribution observed. The hydroxyl termination mechanism was confirmed by $^1$H NMR spectroscopy analyses of the terminal structure of the polymer obtained with the supported copper triflate catalyst (without solvent, peak at $\delta = 4.2$ ppm for the hydroxyl end –CH–OH).

In all the previous experiments, the molecular weight of the polymer obtained with the silica-supported copper triflate catalyst is much lower than the theoretical one (calculated $M_n = 90{,}600$). Despite the high initiation rate, transfer reactions by $\beta$-proton abstractions from the growing polymer chain could also frequently occur. A possible transfer reaction from the counteranion (hydroxyl group) leads to polymer chains with terminal unsaturations (confirmed by IR spectroscopy on the polymer, band at 965 cm$^{-1}$ [22]) and can regenerate an active species, capable of further initiation, thus the high conversion. Transfers from surface silanol groups and monomer can also be considered, although the former results in a cation inactive in the initiation.

Two different processes are therefore responsible for the termination of the growing polymer chain: termination and transfer, producing polymer with hydroxyl end groups and terminal unsaturations, respectively. The contribution of each of these processes depends mainly on the reaction conditions but it is believed that both counteranion and monomer transfer, with catalyst regeneration and formation of a monomer cation, respectively, might predominate as high conversions are obtained.

### 3.4. Successive monomer additions

Complete conversions can be easily achieved with supported copper triflate catalysts, giving, however, low molecular weight polymers. The combination of high initiation and transfer rates is believed to be responsible for the high conversion, consuming all the monomer units before the formation of long polymer chains can occur. Further polymerization should therefore be possible upon monomer addition if some initiating and growing species are still present in the polymerization system.

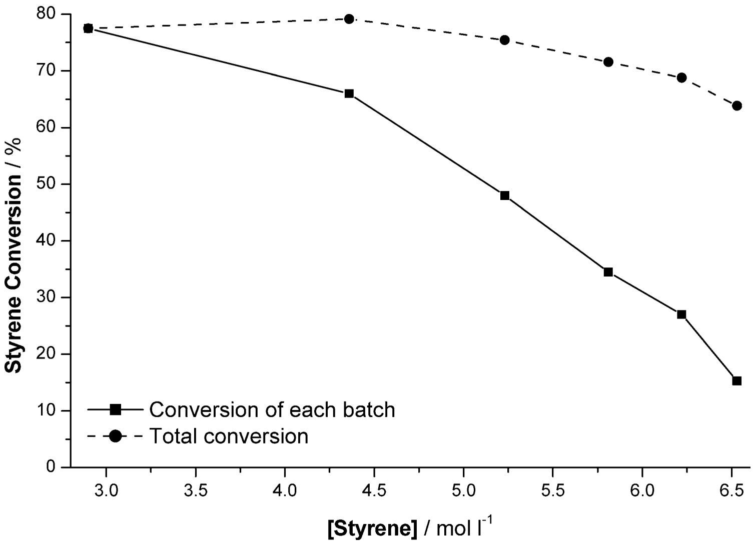

Fig. 8. Batch polymerization of styrene initiated by Cu(OTf)$_2$-K100. Polymerization was carried out in toluene (10 ml) and started with 43.56 mmol of styrene at a concentration of 2.9 mol L$^1$, and 0.5 g of catalyst (0.1 mmol g$^{-1}$).

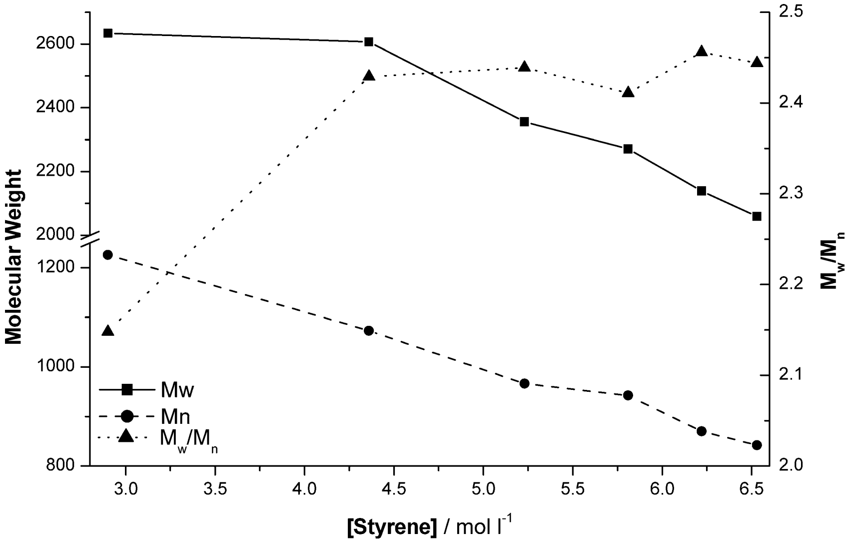

Fig. 9. Batch polymerization of styrene initiated by Cu(OTf)$_2$-K100.

Fig. 8 presents the conversion profile of the successive addition of monomer to the reaction media. The polymerization was carried out in toluene in order to provide thorough mixing throughout the reaction. A new batch of monomer (5 ml) was added to the reaction medium every hour. The conversion of each new batch was deducted from the total conversion measured 1 h after each batch addition.

Progressively decreasing conversions were obtained for each batch of monomer. Initiating and/or growing active species are therefore still present in the system. A final total conversion of 64% was achieved, giving a turnover number (TON) of 3345. However, if only 13% of the active sites are considered to be active (see Section 3.3.1), the value of the TON is 25732.

The molecular weight also decreased progressively with each monomer addition, whereas the polydispersities remained nearly constant, as shown in Fig. 9. New polymer chains were therefore formed at each monomer addition without or with little further growth of the already existing polymer chains. The rate of transfer reaction is then substantial in the polymerization, as nearly each polymer chain formed by rapid initiation is terminated. However, this rate stays constant with each monomer addition, as similar polydispersities are obtained.

The progressive loss of activity observed might be due to the accumulation of polymer in the reaction system. Blocking of the catalyst pores then occurs, preventing the diffusion of the monomer to the initiating active species. Indeed, analyses of the supported catalyst after use by nitrogen adsorption, STA, and DRIFT show the presence of polystyrene on the catalyst as well as within the pores.

### 3.5. *Catalyst reuse*

To overcome the problem of the poisoning of catalyst previously discussed, the polymer/monomer mixture was removed from the reaction media by decanting after the reaction was allowed to settle. The catalyst was washed several times with toluene before addition of more monomer. The results for such catalyst reuse are presented in Table 3. As for the continuous polymerization, a decrease in the monomer conversion, more significant here, is obtained, and very similar molecular weight is observed. A TON of 1010 is achieved (TON = 7780 if considering only 13% of active sites), indicative of a large decrease in active sites compared to the "continuous" polymerization.

From the analyses of the catalyst after use, it was demonstrated that some polymer chains persist on the catalyst surface even after washing. Both poisoning of the active sites and poorer diffusion of the monomer to the residual active sites due to partial pore blocking reduce the initiation rate, together with the elimination of the growing species and monomer cation (from monomer transfer) during the washing process.

Table 3
Polymerization of styrene initiated by Cu(OTf)$_2$–silica catalysts[a]

| Use | Conversion,% | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| 1 | 77.5 | 1160 | 2.30 |
| 2 | 35.6 | 1280 | 2.16 |
| 3 | 3 | – | – |

[a] Polymerization carried out in toluene (10 ml) at 22 °C using 43.56 mmol styrene at a concentration of 2.9 mol L$^{-1}$; [Cu(OTf)$_2$]$_0$ = 0.115 % mol (0.1 mmol g$^{-1}$ catalyst pretreated at 600 °C), for each use.

## 4. Conclusion

Copper triflate is an efficient catalyst in the cationic polymerization of styrene. However, its grafting onto a silica surface enhances the overall reactivity of the catalyst: faster conversions are observed and polymers with higher molecular weight are produced. Little leaching of species from the supported catalyst is observed. The initiation with

$Cu(OTf)_2$–silica catalyst occurs via a catalyst/cocatalyst process between the Lewis acid species and mostly the water present in the system. The latter originates from both the hydration water molecules of $Cu(OTf)_2$ and from adventitious moisture. The surface silanol groups of the catalyst and the physisorbed solvent (methanol) from the catalyst preparation can also play a cocatalytic role. Broad polymer molecular weight distributions are obtained as a result of the multiple nature and location of the active sites including those in and out of the pores. The water molecules not only facilitate the initiation but have also a tremendous effect on the molecular weight. Indeed, the hydroxyl anion formed during the initiation can act as both terminating and transfer agents, forming hydroxyl and unsaturated end groups, respectively. Proton transfers to the monomer also participate in the formation of polymer chains with unsaturated end groups. The resistance of $Cu(OTf)_2$–silica toward water and air exposure allows its use in a continuous process as well as its reuse. However, the presence of some polymer chains trapped within the pores of the catalyst, even after washing, reduces the diffusion of the monomer to the active sites, and thus the initiation rate. In addition, it has been shown that the accumulation of unsaturated polymer chains also poisoned the active sites. Nevertheless, high TON can be obtained in a continuous polymerization system.

It is worth stating that it has not been the aim of this paper to focus on the characteristics of the polymers produced (molecular weights, molecular weight distribution), but more to demonstrate the viability of the $Cu(OTf)_2$–silica material as a solid Lewis catalyst for polymerization processes.

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