Polymerisation of styrene using Y, USY and β zeolites as catalysts

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The homopolymerisation of styrene is studied in the presence of Y, USY and beta zeolites. High molecular weight polymers, in the range 0.7×10^6–1×10^6, are obtained in good yields. The activity of zeolite beta is only slightly increased by calcination of the as-synthesised material, pointing to an important role of the zeolite outer surface. The influence of the catalyst acidity upon the polymer molecular weight is evaluated by the use of dealuminated zeolites.

Keywords: beta, polymerisation, polystyrene, styrene, USY, zeolites

1. Introduction

The acid-catalysed oligomerisation of lower olefins is an important refinery operation used to convert light olefin-rich gases into gasoline range hydrocarbons [1]. Zeolites, due to their characteristic strong acidity, have been used to some extent as catalysts in the oligomerisation of that type of monomers [2–8]. However, the use of these crystalline solids to obtain high molecular weight polymers is barely reported in the literature, the work of Ismayel et al. [9] being relevant in the polymerisation of ethylene.

In this work we report the homopolymerisation of styrene to high molecular weight polystyrene, catalysed by Y, USY and β zeolites. The effect of the zeolite external surface and hydrothermal treatments on the conversion and chain length of the polymer is evaluated. The behaviour of these catalysts is compared with that of amorphous silica–alumina, bearing in mind that styrene thermal (non-catalysed) polymerisation is a competitive reaction.

2. Experimental

Zeolite beta was synthesised according to Wadlinger et al. [10]. Calcination to remove the organic template was performed at 500 °C. Samples of zeolite beta were used uncalcined, keeping the organic template inside the zeolite pores (samples β 20* and β 40*; the numbers denote the Si/Al ratios), or calcined, in which the organic template was removed (samples β 20 and β 40).

The Y catalyst samples were prepared using zeolite LZY62 (ammonium form, Aldrich) as starting material. The parent material was treated with ammonium nitrate as follows: the samples were suspended in a 2 M NH_4NO_3 solution and heated at 80 °C under continuous stirring for 1 h, washed with water and dried at 100 °C to a freely flowing powder. Finally, the catalyst samples were converted into the hydrogen form by calcination at 550 °C for 3 h.

Samples named USY 500 and USY 700 were prepared by hydrothermal treatment of the Y parent material, at atmospheric pressure (100% steam) for 3 h at 500 and 700 °C, respectively. After each hydrothermal treatment the zeolite samples were exchanged twice with ammonium nitrate and converted into the hydrogen form as described above.

Amorphous silica–alumina (SA) (from Aldrich) was converted into the protonic form using the same procedure as described above for the Y and USY samples.

X-ray diffraction was carried out on a Rigaku D/MAX III C diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å).

Surface areas and pore volumes were obtained from the nitrogen adsorption isotherms, measured at 77 K, in a Micromeritics ASAP 2010 V1.01 B instrument.

The total aluminium and silicon contents of the catalyst samples were obtained by atomic absorption using a Perkin-Elmer 2380 AA spectrometer.

The polymerisation reactions were carried out in magnetically stirred microvials (5 cm^3), in which solutions of 20 mmol of polymerisation grade styrene (Shell Co.) in toluene (1.25 cm^3) were added to the catalyst (0.5 wt% on monomer). These reactions were performed at 90 °C, in air, with reaction times of 4 and 24 h, respectively, and were stopped by pouring out the reaction mixtures into a large excess of methanol.

Molecular weight determinations were measured in a SEC apparatus (Waters) at 30 °C, using a series of three columns (Waters Ultrastyragel), 10^3, 10^4 and 10^6 Å and chloroform as eluent.

^{1}H and ^{13}C NMR spectra of the obtained polymer samples in 1,2-tetrachloroethane-d_2 were measured at 300 and 75.47 MHz, respectively, on a Varian Unity 300 spectrometer at 120 °C. The microstructure determinations (P_m) of the

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polystyrene samples were performed by the triad analysis of the *ipso* carbon resonance [11].

3. Results and discussion

Table 1 shows the polymer yields after 4 and 24 h of reaction, the weight average molecular weight, $\overline{M}_\mathrm{w}$, and polydispersity, $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$ ($\overline{M}_\mathrm{n}$, number average molecular weight) of polymers obtained for all the catalyst samples tested.

The polymer yield after 4 h of reaction can be used as an indication of the catalytic activity of the zeolites. After 24 h, the viscosity of the reaction mixture is very high and diffusional limitations are relevant.

The catalytic activity of the uncalcined zeolite beta, with an organic template filling the pores, is approximately half of that observed for the calcined beta (table 1). Simultaneously, the removal by calcination of the organic template used in the zeolite synthesis leads to a strong increase of its total surface area (table 2). Although we are dealing with polymerisation reactions, yielding large macromolecules, these findings indicate that a fraction of the zeolite internal surface area seems to have some catalytic effect.

When Y and USY zeolites are used, the polymer yield after 4 h decreases in the order HY $>$ USY 500 $>$ USY 700. On the other hand, the average molecular weight increases in the same order HY $<$ USY 500 $<$ USY 700 (table 1), while the number of Brønsted acid centres, related to the number of framework aluminium atoms per unit cell (N_Al, table 2), decreases in the same order. These results suggest that the Brønsted acid sites are somehow responsible for the initiation step of the polymerisation reaction, possibly through a cationic mechanism. The observation that the polymer molecular weight decreases when the number of active sites increases can be attributed to higher rates of chain transfer and/or termination reactions [9].

Table 1
Polymerisation of styrene catalysed by beta, Y and USY zeolites and amorphous silica–alumina. Yields at 4 and 24 h of reaction, weight average molecular weight and polydispersity at 24 h of reaction (styrene, 20 mmol; solvent, toluene, 1.25 cm^3; $T = 90\,^\circ$C; catalyst, 0.5% monomer weight).

Zeolite	Yield (%)		$\overline{M}_\mathrm{w} \times 10^{-5}$	$\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$
	4 h	24 h	(24 h)	(24 h)
β 20*	6.6	34.1	7.56	1.66
β 40*	5.2	26.5	7.78	1.75
β 20	11.6	18.2	5.22	1.83
β 40	13.5	17.6	6.37	2.06
SA	39.8	82.8	0.01	1.51
HY	9.6	30.5	5.37	2.19
USY 500	5.7	16.2	6.80	1.75
USY 700	5.1	24.5	10.50	2.27
–	21.3	39.0	5.51	1.93

*As-synthesised – with the template inside.

The decrease in the activity may be due not only to the decrease of the number of Brønsted sites, but also to the obstruction of the zeolite pores by extra-framework aluminium species (EFAl). As it has been shown by recent MAS-NMR studies, EFAl species generated in zeolite Y by hydrothermal treatment are mainly formed by penta- and hexacoordinated aluminium [12]. These species are responsible for an increase in the Lewis acidity [12]. However, in the case of styrene polymerisation, it is not likely that EFAl species play a relevant role.

The catalytic activity observed for uncalcined zeolite beta is smaller than that observed for calcined samples, due to a smaller number of available active sites, whereas the corresponding polystyrene average molecular weights follow a reverse order (tables 1 and 2). The higher number of active sites in the calcined catalyst in relation to the uncalcined one leads to an increase of the chain transfer and/or termination reactions and, hence, to a product of lower molecular weight.

Among all the catalyst samples tested, amorphous silica–alumina shows the highest catalytic activity (39.8%, table 1). A much higher surface area accessible to styrene and, therefore, a much larger number of accessible active sites can explain this behaviour. In the case of zeolites, the fraction of the surface area corresponding to micropores is dominant. In principle, this micropore area is initially accessible to styrene, but once oligomers are formed in the zeolite pores, they would become unable to diffuse outside due to the small pore diameter (~7 Å for beta and Y zeolites [13]). Thus, we may envisage that diffusion of propagating species to the outside of the zeolite particle

Table 2
Physicochemical characterisation of the zeolite samples used as catalysts in styrene polymerisation.

Sample	Si/Al$^\mathrm{a}$ (total)	Crystallinity$^\mathrm{b}$ (%)	$N_\mathrm{Al}$$^\mathrm{b}$	Aver. pore diameter (Å)	Surface area (m^2/g)	Micropore area (m^2/g)	Ext. surf. area (m^2/g)	Pore volume (m^2/g)
β 20*	20	–	–	–	54.1$^\mathrm{c}$	16.9	37.2	0.049
β 40*	40	–	–	–	–	–	–	–
β 20	20	–	3.0$^\mathrm{e}$	16.6	753.3$^\mathrm{c}$	638.0	115.3	0.312
β 40	40	–	1.6$^\mathrm{e}$	–	–	–	–	–
SA	–	–	–	62	451.2$^\mathrm{c}$	19.8	431.5	0.665
HY	2.6	100	46.4	16	849.4$^\mathrm{d}$	757.9	91.5	0.351
USY 500	2.9	82	36.7	19.3	803.7	715.1	88.7	0.388
USY 700	3.0	61	21.8	21.5	728.3$^\mathrm{d}$	647.7	80.6	0.391

$^\mathrm{a}$Atomic absorption. $^\mathrm{b}$XRD. $^\mathrm{c}$BET isotherm. $^\mathrm{d}$Langmuir isotherm. $^\mathrm{e}$Estimated assuming 100% crystallinity.

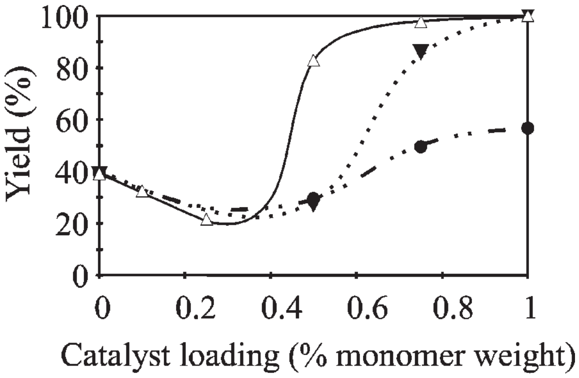

Figure 1. Effect of the catalyst loading on the polymer yield. (●) USY 700; (▲) β 40; (△) amorphous silica–alumina.

would occur exclusively from a thin outer spherical layer which is likely to correspond to the available catalytic area.

Oppositely to what occurs with zeolites, the amorphous silica–alumina external surface area (external surface plus meso- and macropores) is the dominant fraction of the total surface area (table 2). As the pore diameter is now high ($\sim$62 Å, table 2), these pores do not become blocked as easily as in the case of zeolites. Since the accessible catalytic area and, therefore, the number of accessible active sites is much higher than that of zeolites, a higher incidence of transfer and/or termination reactions is favoured, leading to an oligomeric polystyrene.

A blank reaction corresponding to the styrene thermal (non-catalysed) polymerisation was performed, leading to polystyrene with a molecular weight of 5.5×10^{-5} and 39% yield after 24 h (table 1). This means that thermal polymerisation occurs to a significant extent, the corresponding $\overline{M}_{\mathrm{w}}$ being similar to those of experiments carried out with β 20 and HY, but significantly less than the values obtained for the rest of zeolites. The dependence of the polymer yield after 24 h reaction on the catalyst loading is shown in figure 1. For low catalyst loadings, in the range of 0–0.5% of the monomer weight, the polymer yield decreases as the amount of catalyst increases. On the other hand, for catalyst loadings in the range of 0.5–1%, the yield increases with the amount of catalyst, reaching 100% for the catalyst samples β 40 and SA. These results and the above-discussed trends in yield, $\overline{M}_{\mathrm{w}}$ and available catalytic surface, suggest an inhibition of the thermal polymerisation in the presence of zeolites or amorphous silica–alumina, particularly evident for low catalyst loadings. When catalyst contents higher than 0.5% of the monomer weight are used a positive catalytic effect is observed.

All the polymer samples exhibit atactic microstructures ($P_{\mathrm{m}} = 0.48$–0.50) as determined by ^{13}C NMR.

4. Conclusions

The results obtained suggest that the zeolites tested are active in the homopolymerisation of styrene. Although thermal polymerisation occurs as a competitive reaction, only with zeolites was it possible to achieve values of $\overline{M}_{\mathrm{w}}$ as high as 1×10^6.

Zeolites and amorphous silica–alumina seem to have an inhibition effect on the thermal polymerisation. However, the experiments performed with increasing amounts of catalyst showed unequivocally a positive catalytic effect on the polymerisation reaction.

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