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Monolithic catalysts for the fixed-bed hydrogenation of polymers

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Monolithic catalysts were successfully applied in a true fixed-bed hydrogenation of polymers such as SBS rubbers and polystyrene.

Styrene–butadiene–styrene (SBS) tri-block polymers have been industrially hydrogenated for some 30 years. They are presently sold by KRATON Polymers as high-value elastomers with improved UV and temperature stability.[1] The hydrogenation process proceeds on a highly viscous polymer solution using colloidal nickel/aluminium catalysts at 80 °C and 60 bar hydrogen.[2–5] More recently Dow Chemicals commercialised fully hydrogenated styrenic block copolymers,[6] which are hydrogenated using micron-size catalyst particles that are slurried in the polymer solution.[7] In both cases, however, is it difficult and expensive to recover the catalyst residues from the concentrated and viscous polymer solution or slurry. Alternative catalysts to alleviate this problem would be of great interest. Truly homogeneous catalysts[8,9] are, obviously, not easier to recover. Conventional heterogeneous catalysts require a high reaction temperature of ~200 °C,[8,10] which unfortunately results in reduction of the molecular weight of the product. In contrast, we report here our successes in hydrogenating polymer solutions with monolithic megaporous catalysts without degrading or contaminating the product.[11] These catalysts structures—with pore diameters >0.1 mm rather than <100 nm–include foams, honeycombs, corrugated sheets (stacked or rolled) as well as wire mesh.[12–14] They have been especially designed to offer minimal resistance to flowing gases, for example in gas treating devices for power plants and car exhaust pipes, but their potential in viscous media has not yet been recognised.

The monolithic catalysts were supported on α-alumina foams† that contained cellular pores of ~1 mm diameter and were cut as cylinders of 50 mm height and 55 mm diameter (65 g). A hole was drilled axially through the cylinder to accommodate the axle of an autoclave stirrer, to which it was mounted for catalytic evaluation. A few samples with higher specific surface area comprised monolithic α-alumina foam with a 5–6 wt% "HPA" porous wash-coat, a blend of calcined hydrated alumina.† The catalysts were prepared by impregnation of the foam with a solution of Ni, Cu or Pt with subsequent calcination at 500 °C‡. The alumina foam was mounted on the stirrer of a 250 mL autoclave. The supported metal oxide phase was reduced to the metallic state by passing hydrogen through the autoclave at 200 °C. After cooling to room temperature, 160 g of a 5–10 wt% solution of Kraton®-D SBS polymer (M_w 71 600) in cyclohexane was added and the autoclave was pressurised with 60 bar hydrogen. The autoclave was heated to 120 °C and held at this temperature for 8 h, with the monolith spinning in the polymer solution at 800–1200 rpm. The resulting polymer was isolated by evaporation of the solvent in a steam-bath and, subsequently, under vacuum at 30 °C overnight. Conversion and selectivity were determined by ^{1}H NMR spectroscopy. Gel-permeation chromatography (GPC) and ICP-MS analysis of the products were carried out to ensure the integrity of the polymer backbone and quantify potential metal residue in the polymer, respectively. The same catalyst foam was reused for subsequent reactions, after being reduced again as described above.

The foam impregnated with 5 wt% Ni was evaluated according to a fractional design constructed on the following operational window: 90–120 °C, 40–60 bar, 800–1200 rpm for 4–8 h with a solution that contained 5–10 wt% polymer. According to the selected data reported in Table 1, the alkene functions present in the butadiene mid-block were hydrogenated up to 64% while the aromatic rings of the styrene end-blocks where hydrogenated up to 41%. The reaction temperature and H_2 pressure were important variables in determining the conversion degree. However, these parameters did not significantly affect the butadiene:styrene hydrogenation selectivity—typically between 1.5:1 and 2:1 (see closed diamonds in Fig. 1). It should be stressed that all these runs were carried out using the same catalyst sample and that no significant sign of deactivation was observed after 5 runs (compare 2/1 and 2/5). Analysis of the polymer solution did not reveal detectable amounts of Ni or changes in molecular weight.

The deposition of a wash-coat on the monolith prior to impregnation with 5 wt% Ni resulted in a two-fold increase in hydrogenation activity without significantly affecting the hydrogenation selectivity between the butadiene and styrene blocks (compare 3/1 with 2/1 in Table 1 as well as the open diamonds with the closed diamonds in Fig. 1).

The foam impregnated with 5 wt% Cu showed activity for hydrogenating the butadiene block similar to that of the Ni-based catalyst. Interestingly, it showed no measurable activity for hydrogenating the styrene end-blocks (see run 5/1 in Table 1 and closed triangle in Fig. 1), resulting in a selective catalyst.

The foam impregnated with 1 wt% Pt yielded conversions and selectivities comparable to the Ni-impregnated foams (see Table 1

Table 1 Hydrogenation of an SBS rubber (Mw 71,600) with metal catalysts supported on an alumina foam

Run	t/h	T/°C	P/bar	SBS (wt%)	Mix/rpm	X_{BD}[a] (%)	X_S[a] (%)
5 wt% Nickel impregnated foam							
2/1	4	120	40	10	1200	27	10
2/2	8	90	40	5	1200	28	13
2/3	8	90	40	10	800	21	9
2/4	8	120	60	5	800	64	41
2/5	4	120	40	10	1200	26	11
5 wt% Nickel impregnated wash-coated foam							
3/1	4	120	40	10	1200	44	14
3/2	8	120	60	10	1200	72	33
1 wt% Platinum impregnated wash-coated foam							
4/1	4	120	50	10	1200	39	24
4/2	4	160	50	20	1200	43	10
4/3	8	160	50	10	1200	58	43
5 wt% Copper impregnated foam							
5/1	7.5	120	60	10	1200	60	0

[a] X_{BD} and X_S represent the butadiene and styrene conversion.

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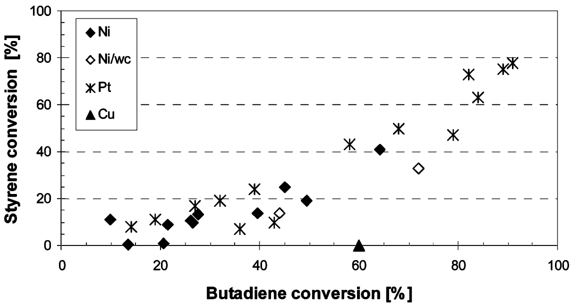

Fig. 1 Hydrogenation of an SBS rubber over various metal catalysts supported on an alumina foam (90–190 °C, 40–60 bar H_2, 4–24 h).

and compare stars with diamonds in Fig. 1). At high conversion, the product slowly separated in two phases with different conversion degrees. For instance, the product from run 4/3 (Table 1) segregated in an upper phase with 68% butadiene conversion (50% styrene conversion) and a bottom phase with 32% butadiene conversion (19% styrene conversion). Further purification of this product by dissolution in *n*-decane–toluene and subsequent precipitation with acetone yielded a fully saturated polymer fraction, with >98% hydrogenation of both butadiene mid-block and styrene end-blocks. Obviously, some polymer chains are more deeply hydrogenated than others. Similar observations have been reported previously[8] and can be explained by the slow diffusion of the macromolecules, which favours multiple hydrogenation once they have entered the catalyst pores.

Consistent with the results obtained with the monolithic Ni catalyst, the monolithic Cu and Pt catalysts did not lead to measurable changes in molecular weight nor detectable amounts of metal in the polymer product.

We were interested in extension to the hydrogenation of polystyrene to poly(vinylcyclohexane) as this has been reported to result in a significant increase in the glass-transition (T_g) temperature of the material.[15] To this end, we prepared a polystyrene polymer with M_w of ~35 000 and contacted it with the spent Pt-based catalyst for 8 h under 50 bar hydrogen at 180 °C. DSC analysis of the polystyrene and its hydrogenated product revealed a shift of onset T_g, from 95 °C for the polystyrene precursor to 128 °C for its hydrogenated product. This confirms the potential of monolithic catalysts for upgrading polymeric materials.

We have shown that the deposition of an active metal onto a megaporous monolithic support yields catalysts that (1) enable the hydrogenation of polymers and (2) can be easily recovered without contaminating the polymeric product. The choice of metal is, obviously, critical in determining the activity and selectivity of the monolithic catalyst. However, proper selection of reaction parameters, such as temperature, pressure or solvent is also expected to affect the reaction selectivity. The application of monolithic catalysts for upgrading polymers is obviously not limited to hydrogenation reactions. Monolithic materials with acidic, basic or redox properties are also expected to enable the modification of polymeric materials as do homogeneous catalysts.[8]

Notes and references

† The foams, including the 'HPA' washcoat, were purchased from Hi-Tech Ceramics (NY/USA). The porosity was 20 pores per inch.

‡ *Catalyst preparation*: 3.2 g Ni or Cu (as nitrates) or 0.7 g Pt (as H_2PtCl_6) were dissolved in 15 g distilled water. The carrier (65 g) was (1) dried at 120 °C for 1 h, (2) impregnated with 10 g solution delivered dropwise, (3) dried again, first using a hairdryer and then in an oven at 140 °C for 30 min, (4) impregnated further with the remaining 5 g solution and (5) dried at 120 °C for 4 h and at 500 °C for 1 h.

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