The catalytic oxidation of cyclohexanone to caprolactone using hexagonal mesoporous silica supported SbF_3 †

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L e t t e r

The solid acid catalyst SbF_3 supported on hexagonal mesoporous silica is an active and reasonably selective catalyst for the oxidation of cyclohexanone to caprolactone using hydrogen peroxide.

The Baeyer–Villiger oxidation of ketones to lactones or esters is a widely used synthetic method and was comprehensively reviewed in 1957 by Hassall[2] and in 1993 by Krow.[3] The most common reagents used for this reaction are peroxycarboxylic acids (*e.g.* peracetic acid, *m*-chloroperbenzoic acid). These are commercially available on a large scale, but their industrial use is either costly or requires significant safety considerations. They are shock sensitive in their pure form and may be explosive in the condensed phase and, in practical use, acidic or halogen based solvents are required. Moreover, they yield the corresponding carboxylic acids, raising separation and recycling concerns. In order to avoid the use of these potentially dangerous materials and to lower the environmental impact of the waste produced, various other oxidation systems using hydrogen peroxide as the oxidant have been developed.[4–6] The oxidation of cyclohexanone to ε-caprolactone is of particular industrial interest since the product is extensively used in the synthesis of polycaprolactones.[7] In this article, we wish to report a new efficient heterogeneous catalytic system for the Baeyer–Villiger oxidation of cyclohexanone by hydrogen peroxide, using a novel catalyst: antimony trifluoride supported on hexagonal mesoporous silica (HMS).

Tanabe and Hattori have made solid superacids based on silica (or other metal oxides) supported antimony pentafluoride,[8] but to the best of our knowledge, SbF_3 (easier to handle and safer than SbF_5) supported on silica has never been reported. The resulting materials are not superacidic, as measured by Hammet indicators ($-2 < H_0$).

The HMS support was synthesised according to the method described by Tanev and Pinnavaia,[9] using 1-aminododecane as a template, which was removed either by calcination, leading to support HMS-C, or by ethanol extraction (HMS-E). Straight after calcination, the material was treated with a refluxing mixture of antimony trifluoride in sodium dried toluene, followed by solvent evaporation on a rotary evaporator. The resulting white fine flowing powder (HMS-C-SbF_3) can be handled and stored in air without loss of catalytic activity. In the case where the template was removed by ethanol extraction, the HMS was dried at 120 °C in a vacuum oven for 4 h prior to treatment with antimony trifluoride in refluxing sodium dried toluene (HMS-E-SbF_3). Commercial silica (Merck, Kieselgel 60) was also used as a support after drying under vacuum at 120 °C (K-120-SbF_3) or calcination in air at 600 °C (K-600-SbF_3).

† The content of this Letter is based on the patent described in ref. 1.

The DRIFT (diffuse reflectance infrared fourier transform) spectra of the various catalysts prepared showed no apparent difference to those of underivatised HMS or Kieselgel. Simultaneous thermal analysis (STA) traces of various batches of the catalyst, when compared with pure SbF_3 (which melts at 294 °C and volatilises at 319 °C), suggest that antimony trifluoride reacted with the silica surface to yield as yet undetermined surface species.

The acidic character of the surface of the catalysts was probed *via* pyridine adsorption, which showed that the catalysts possess both Lewis (IR band at 1489 cm^{-1}, presumably due to coordinatively unsaturated antimony centres) and Brønsted acid sites (1540 cm^{-1}, probably due to the polarisation of surface hydroxyl groups by antimony trifluoride).[10,11] In an aqueous environment, the Lewis acid sites can bind water molecules, which will exhibit Brønsted acidity. By potentiometrically titrating aqueous suspensions of the catalysts with sodium hydroxide, the number of acid sites in the catalysts could be determined (Table 1). Both K60 and HMS-C show a very low number of acid sites, while unsupported aqueous SbF_3 is very acidic, each mol of it being titrated by 2.9 mol of hydroxide. This behaviour can be understood from the solid state structure of SbF_3, where three covalently bonded fluorides and three more distant fluorine atoms surround each Sb atom, resulting in a distorted octahedral coordination sphere.[12] When dissolved in water, each molecule seems to keep an octahedral coordination sphere by linking with three water molecules, giving rise to three acid sites.

Regarding the catalysts, at the same loading of antimony trifluoride, fewer acid sites are formed on the calcined silica support than on calcined HMS, possibly due to poorer dispersion of SbF_3 because of the lower surface area of amorphous silica. The drying temperature of HMS's does not seem to significantly influence the concentration of acid sites generated, but the SbF_3 loading does. At a loading of 0.5 mmol g^{-1}, three acid sites are generated per SbF_3 molecule,

Table 1 Number of acid sites on the supported SbF_3 catalysts measured by titration

Material	Loading/ mmol g^{-1}	Number of acid sites/ mmol g^{-1} catalyst
SbF_3	—	16
K60	—	<0.05
K-600-SbF_3	1	1.63
HMS-C	—	<0.1
HMS-C-SbF_3	0.5	1.5
HMS-C-SbF_3	1	1.94
HMS-C-SbF_3	2	3.3
HMS-E-SbF_3	1	2.1

while at 1 mmol g^{-1}, only two acid sites per molecule, and at 2 mmol g^{-1} only *ca.* 1.5 acid sites per molecule are generated. A possible explanation for this could be that antimony trifluoride reacts with silanols to form some surface species, which by polarisation of the surrounding hydroxyls give rise to several Brønsted acid centres. Increasing the amount of antimony trifluoride decreases the amount of available hydroxyls and hence the number of acid sites. An alternative explanation could be the formation of Si–O–SbF$_2$ species on the surface, each accommodating three water molecules to restore an octahedral coordination sphere in the case of the 0.5 mmol g^{-1} loading catalyst, while at higher loadings, fluorine bridging surface species could lead to a decreased ability to bind water molecules.

The nitrogen adsorption isotherms of the various HMS supported catalysts are consistent with the structure of HMS materials. All the prepared catalysts show a lower surface area than that of the starting material (Table 2), which is understandable since the smallest pores may be blocked by antimony trifluoride. The average pore diameter should therefore be larger than that of the parent material, which is the case when the support was pre-treated at 120 °C, but not when it was calcined. It is worth noting that, as studied on various occasions in our laboratory, refluxing the supports in various solvents does not affect their surface area to a significant extent.

The catalysts show a high efficiency in catalysing the oxidation of cyclohexanone to ε-caprolactone. Excess cyclohexanone was used to allow continuous azeotropic removal of the water under reduced pressure. The catalyst was mixed with cyclohexanone and heated to 70 °C before hydrogen peroxide was added drop-wise over 30 min, using a peristaltic pump. ^{1}H NMR was used to monitor the reaction because of the formation of stable cyclohexanone peroxides, which decompose in GC injectors to give caprolactone, cyclohexanone and other products.[13] As a consequence, it was not possible to monitor cyclohexanone consumption (^{1}H NMR peaks of cyclohexanone and its peroxides overlap) and no selectivity figures could be obtained. Background reactions with no catalyst and with underivatised HMS were carried out. Under those conditions, cyclohexanone oxidation did not occur to more than 2% (based on the amount of hydrogen peroxide introduced) after 6 h. Homogeneous antimony trifluoride did catalyse the reaction, but the kinetics of the oxidation was much slower than with supported antimony trifluoride (Fig. 1).

At equivalent SbF$_3$ loading and support pre-treatment, HMS supported catalysts are more efficient than their Kieselgel analogues (Fig. 1), possibly because of their higher surface area. The main by-products identified were polycaprolactone, hydroxycaproic acid and cyclohexanone peroxides.

In a set of reuse experiments, the HMS-E catalyst did not lose its activity, but actually got slightly more active from one run to the other, increasing the caprolactone yield from 27% to 33% between the first and third use of HMS-E-SbF$_3$.

Table 2 Surface areas and average pore size diameters of the supported SbF$_3$ catalysts

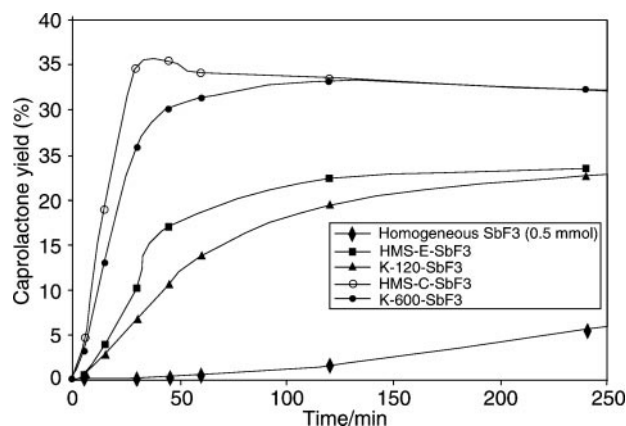| Material	Loading/ mmol g^{-1}	BET surface area/m^2 g^{-1}	Average pore diameter/nm
Kieselgel 60	—	529	5.7
K-120-SbF$_3$	1	383.5	5.9
K-600-SbF$_3$	1	395	5.7
HMS-C	—	1151	3.05
HMS-C-SbF$_3$	0.5	835	3
HMS-C-SbF$_3$	1	843	2.98
HMS-C-SbF$_3$	2	712	2.95
HMS-E	—	1254	3.7
HMS-E-SbF$_3$	1	998	4.1

Fig. 1 Rates of formation of caprolactone from cyclohexanone using various SbF$_3$-based catalysts, at a loading of 1 mmol g^{-1} (yields based on total amount of H$_2$O$_2$ introduced).

Unfortunately, other reuse studies with different batches of HMS-E and HMS-C catalysts at various loadings failed to confirm this behaviour. In every case, the catalyst gradually lost activity from run to run, probably because of polymer formation on the surface of the catalyst, as shown by DRIFT and STA studies. A ^{19}F NMR spectrum of the reaction liquor after filtration did not show any fluorinated species, suggesting that no antimony trifluoride leached and that no fluorinated organics were produced during the reaction.

The effect of support treatment prior to reacting antimony trifluoride with its surface is very important for the catalytic properties of the resulting material. With SbF$_3$ supported on calcined HMS, better yields of caprolactone can be obtained than with SbF$_3$ supported on HMS dried at 120 °C. Both the water content of the support and the nature of its surface before SbF$_3$ grafting are important to the final catalytic properties (if HMS materials behave like silica, the calcined HMS surface should mainly present siloxane bridges,[14] as opposed to silanols for the HMS dried at 120 °C).

When HMS-C-SbF$_3$ is used, caprolactone production stops about 15 min after the end of hydrogen peroxide addition. The decrease in caprolactone yield after that time is due to its conversion to hydroxycaproic acid and low molecular weight polycaprolactone (caprolactone oligomers). The analysis of the reaction mixture at 60 min shows that its active oxygen content is less than 1%, indicating that most of the hydrogen peroxide has reacted.

Variation of the quantity of catalyst (HMS-C-SbF$_3$) at 70 °C showed that the reaction rate is dependent on the amount of catalyst used, but that the quantity of polycaprolactone and hydroxycaproic acid produced is even more influenced by this factor. Hence, larger quantities of catalyst lead to poor caprolactone yield and high yields of hydroxycaproic acid and polycaprolactone (Fig. 2).

The effect of the SbF$_3$ loading on the activity of the HMS-C-SbF$_3$ catalyst has also been investigated. When it is increased to 2 mmol g^{-1}, the initial rate of the reaction is faster and the best caprolactone yield obtained at 70 °C is 40.3% (34.6% with a loading of 1 mmol g^{-1}), but the amount of by-products is also increased. On the other hand, with a lower loading of 0.5 mmol g^{-1}, even though the initial rate of reaction is slightly slower, the yield of caprolactone after 45 min is comparable to that obtained with a 1 mmol g^{-1} catalyst, and by-product formation is halved.

When the reaction is run at 90 °C (130 mbar), the efficiency of the catalysts is even greater, enabling yields of *ca.* 80% of caprolactone to be obtained in 45 min with a 1 mmol g^{-1} catalyst on HMS-C. When taking into account the amount of polycaprolactone formed, it can be calculated that more than 88% of the hydrogen peroxide introduced (it is unfortunately
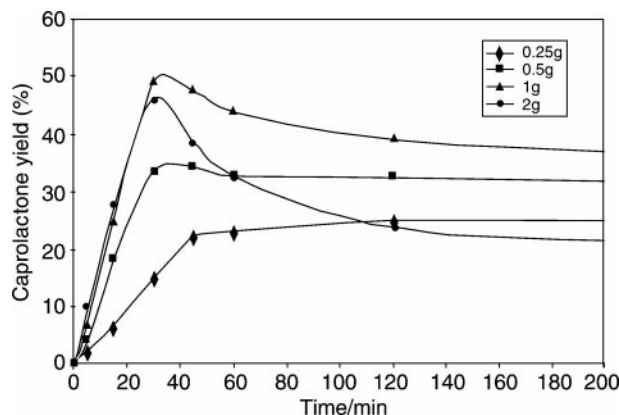
Fig. 2 Effect of increasing the quantity of the HMS-C-SbF$_3$ catalyst on the conversion of cyclohexanone to caprolactone.

not possible to determine accurately the amount of hydroxy-caproic acid formed) has been used for cyclohexanone oxidation to caprolactone.

Increasing the reaction temperature further to 110 °C did not improve the yield, but by using a 0.5 mmol g^{-1} HMS-C-SbF3 catalyst at 90 °C, 76% of caprolactone was obtained while by-product formation was more than halved (overall peroxide selectivity 78%).

We have prepared a new efficient HMS-supported catalyst for the oxidation of cyclohexanone to caprolactone by hydrogen peroxide. Ring opening and polymerisation of the lactone are the main side reactions, and the amount of by-products depends on the reaction time. The catalyst's characterisation is still underway, as is the optimisation of the process for forming caprolactone, and the application of the novel catalyst to other organic reactions.

Experimental

The ^{1}H NMR spectra were recorded on a JEOL EX270 spectrometer. STA traces were recorded using a PL Thermal Sciences STA625 instrument. DRIFT spectra were obtained on a Bruker Equinox 55 FTIR spectrometer. N$_2$ adsorption isotherms, surface areas and pore size distributions were obtained at 77 K on a Coulter SA3100 surface area analyser.

The cyclohexanone (99.8%) and the SbF$_3$ (99.8%) used in this study were obtained from Aldrich and used without further purification. The hydrogen peroxide was provided by Solvay Interox (UK).

HMS preparation

In a mechanically stirred round bottomed flask, 25.47 g of 1-aminododecane were dissolved in 250 ml of ethanol and 250 ml of deionised water. 56 ml of tetraethoxysilane were added to this mixture, resulting in the formation of a gel, which was aged for 24 h, stirring at room temperature. The resulting solid was then filtered and washed with ethanol.

HMS-C: the template was burnt out of the prepared HMS by calcination in air at 600 °C for 7 h.

HMS-E: the HMS was washed in refluxing ethanol and filtered. This washing was repeated three times.

Supported SbF$_3$ catalysts preparation

HMS-C-SbF$_3$: the HMS material was calcined for 7 h in air at 600 °C. On removal from the oven, it was cooled to room temperature in a dessicator containing KOH. It was then added to a reaction vessel containing Na dried toluene (25 ml per gram of HMS). The required amount of SbF$_3$ was added to this suspension (0.18 g per g of HMS for a 1 mmol g^{-1} catalyst, weighed in a glove bag, under N$_2$) and the mixture
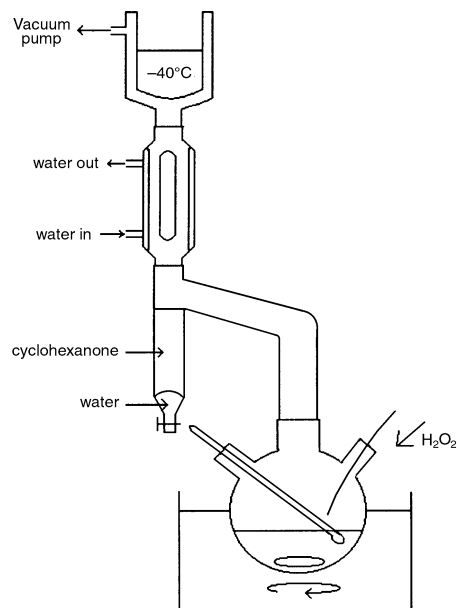

Chart 1

was refluxed for 20 h. The solvent was then removed by evaporation under reduced pressure using a rotary evaporator.

K-600-SbF$_3$: the same procedure was followed using Kieselgel 60 silica (Merck).

HMS-E-SbF$_3$: The same procedure was used, except the HMS-E was dried under vacuum for 4 h at 120 °C instead of calcined.

K-120-SbF$_3$: The same procedure as HMS-E-SbF$_3$ was followed, using Kieselgel 60 silica.

Cyclohexanone oxidation

The experimental set-up used in this reaction is best described by Chart 1.

The vacuum pump used is equipped with a vacuum controller in order to maintain a steady vacuum ($\Delta p = 10$ mbar), and hydrogen peroxide is pumped into the round bottom flask with a peristaltic pump.

In a typical reaction, the Dean–Stark reservoir is filled with cyclohexanone and 25 ml of cyclohexanone are mixed with 0.5 g of the catalyst and 0.5 g of 1,4-dichlorobenzene (internal standard). The mixture is heated to the required temperature under vacuum (70 mbar at 70 °C, 130 mbar at 90 °C), after which hydrogen peroxide addition (4.7 g, 96.7 mmol) is started. At the end of the reaction, the reaction mixture is filtered after cooling and the catalyst is washed with dichloromethane before reuse experiments.

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