

Preliminary study on the TS-1 deactivation during styrene oxidation with H₂O₂

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Abstract

The deactivation of the TS-1 zeolite during styrene oxidation with H₂O₂ has been investigated by a series of kinetic experiments and further characterisation of the spent catalysts. A decline of the TS-1 activity with time has been observed, especially during the first hours of reaction. TG and TPD–MS analyses of the spent catalysts show that the main products occluded within the zeolite pores are styrene, phenylacetaldehyde and benzaldehyde. The presence of styrene oligomeric compounds has also been detected, although it is postulated they are formed mainly in the solution outside the zeolite pores. Diffusional hindrances due to the high degree of occupancy of the TS-1 pores, as well as, a strong adsorption of styrene, phenylacetaldehyde and benzaldehyde on the Ti sites are proposed as the main reasons for the TS-1 deactivation. These phenomena are enhanced at lower reaction temperatures, which cause a faster initial deactivation. Likewise, longer reaction times favour preferential chemisorption of aldehydes versus styrene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Styrene oxidation; H₂O₂; TS-1 zeolite

1. Introduction

TS-1 zeolite is a very efficient catalyst for the oxidation of a variety of organic compounds with H₂O₂: alkane oxyfunctionalisation, phenol hydroxylation, olefin epoxidation, alcohol oxidation, etc. In contrast with the huge research effort focused in the recent years to find out new catalytic applications of this material, almost no papers can be found in the open literature dealing with the TS-1 deactivation [1], although this is a very important factor regarding its

possible commercial application. In this paper, we report a study about the deactivation of the TS-1 zeolite during the styrene oxidation using H₂O₂ as oxidant.

2. Experimental

TS-1 zeolite was synthesised with Si/Ti=62 by the wetness impregnation method from a SiO₂–TiO₂ xerogel [2,3] under microwave radiation [4]. The sample obtained is 100% crystalline with spherical crystals and sizes around 1.35 μm.

Styrene oxidation tests were performed in a laboratory scale stirred autoclave reactor, the products being analysed by GC with an FID detector on a capillary column. The kinetic experiments have

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been carried out under the next reaction conditions: (styrene/H₂O₂)_{molar}=2, solvent: acetone (60 wt.%), reaction mass=100 g, catalyst loading=2.5 g, stirring speed=600 rpm, N₂ atmosphere and autogenous pressure. Four different reaction temperatures have been investigated in the range 40–70°C, samples of the products being taken at different reaction times. The H₂O₂ consumption was determined by iodometric titration. After the reaction, the spent catalysts were recovered by centrifugation, being repeatedly washed with acetone. Finally they were room temperature dried by exposure to the ambient air.

Both fresh and spent TS-1 samples were characterised by a number of techniques. Chemical composition of the zeolites was determined by XRF using a Philips PW 1404 spectrometer. XRD patterns were collected on a Philips X'PERT MPD diffractometer with Cu K α radiation and Ni filter. FTIR spectra were recorded with a Nicolet 510P spectrophotometer using the KBr wafer technique. DR UV–Vis spectra were obtained under ambient conditions on a CARY-1 instrument equipped with a diffuse reflectance accessory, BaSO₄ being used as reference. The crystal size was determined by SEM with a JEOL JSM-6400 microscope. Thermogravimetric analysis (TGA) has been performed in a Perkin Elmer TGA-7 thermobalance with a helium flow rate of 20 N ml/min. The temperature was increased from 20 up to 700°C with a heating rate of 20°C/min. TPD–MS of the products present

in the spent catalysts were carried out by flowing 50 ml(STP)/min of He while the sample was heated at 5 K/min. Around 30 mg of the sample was loaded in a U-shaped quartz reactor connected on line with a quadrupole mass spectrometer (BALZERS QMS 200) which allows the analysis of the reactor outlet.

3. Results and discussion

The TS-1 deactivation during the styrene oxidation with H₂O₂ has been investigated through a series of kinetic experiments carried out at temperatures in the range 40–70°C with acetone as solvent. The main reaction products obtained are summarised in the reaction scheme shown in Fig. 1. Styrene oxide (SO) is the primary product expected from the epoxidation of the double bond in the styrene side chain [5]. However, the major product observed in the reaction system is phenylacetaldehyde (PADH), formed by rearrangement of the styrene oxide. Other secondary products also detected include 1-phenyl,1,2-ethanediol (DIOL), formed by water addition to the styrene oxide, and benzaldehyde (BADH), by C–C cleavage.

Fig. 2 shows the time dependence of both styrene and H₂O₂ conversions (Fig. 2a and b) at the four reaction temperatures investigated, the product distribution obtained at 60°C (Fig. 2c), and the selectivity towards phenylacetaldehyde (Fig. 2d), which is the

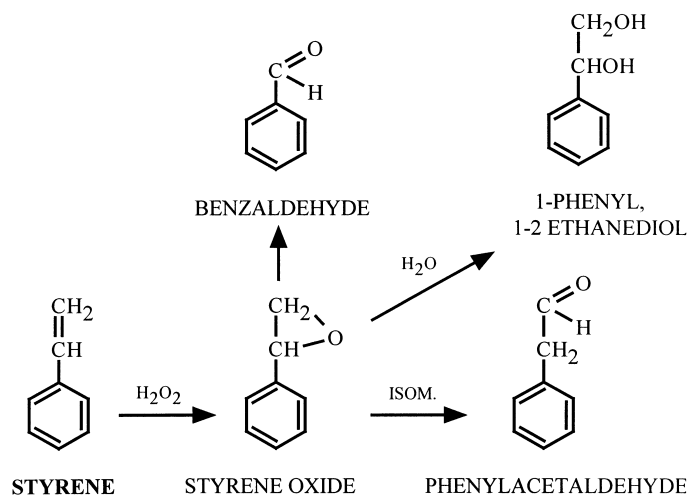


Fig. 1. Reaction scheme of the styrene oxidation with H₂O₂, using acetone as solvent.

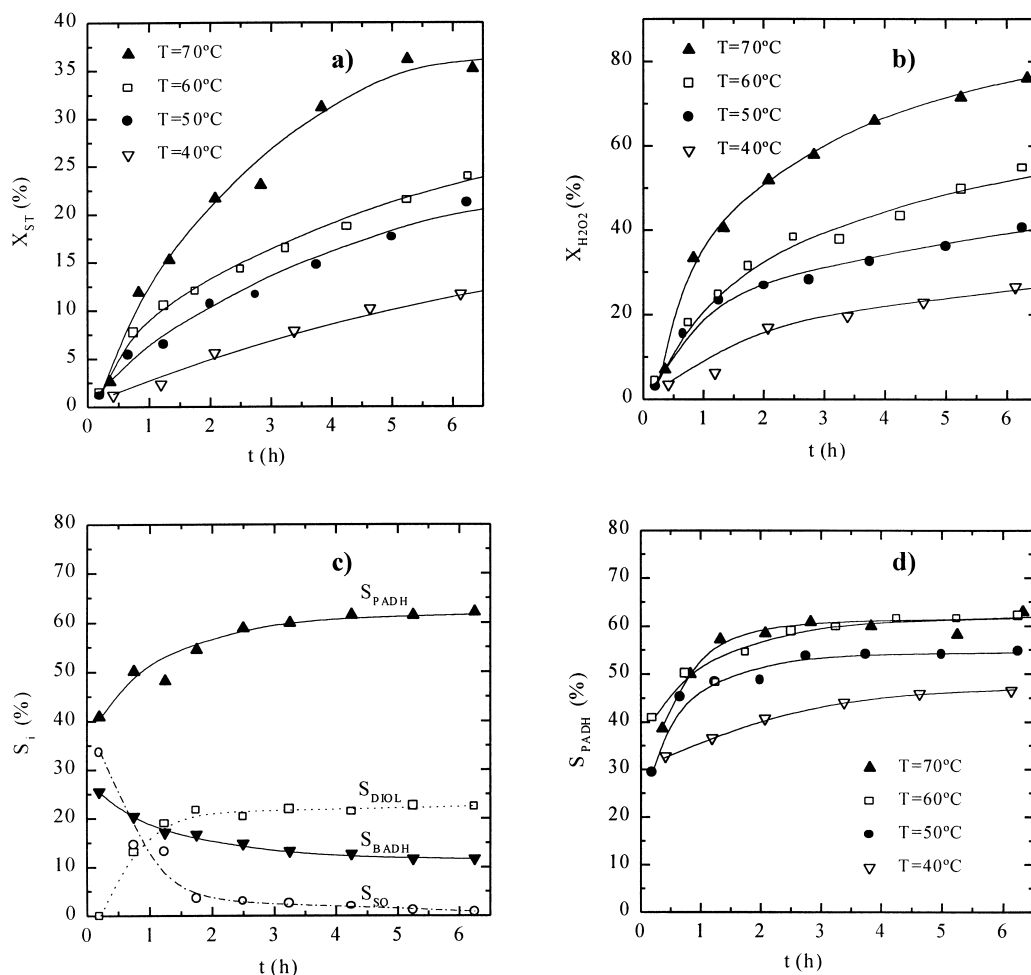


Fig. 2. Kinetic experiments: (a) styrene conversion; (b) H_2O_2 conversions; (c) product distribution; (d) selectivity towards phenylacetaldehyde.

major product obtained in this reaction. As it was expected, the conversion of both reactants, styrene and H_2O_2 , increase with the time and the temperature. In all temperatures investigated, the reaction rate, calculated from the slope of the conversion curves, is higher at the beginning and slows down after 1–2 h of reaction. From this point, the conversion curves seem to tend towards a constant reaction rate. The product distribution obtained at 60°C indicates that the selectivity towards phenylacetaldehyde presents a remarkable increase in the first 2 h of reaction with minor variation from this point. Initially, there is a certain proportion of styrene oxide, but at longer reaction times the major products obtained are phenyl-

acetaldehyde and 1-phenyl,1,2-ethanediol. Likewise, the selectivity towards phenylacetaldehyde is improved as the temperature increases from 40 to 70°C with a limiting value around 60%.

In order to find out whether the decay in the reaction rate observed at the beginning of the kinetic experiments is produced by a deactivation of the catalyst, equilibrium limitations or just to a simple consumption of the reactants, two additional experiments were carried out (Table 1). In the first one, after 3 h of reaction, supplementary amounts of styrene and hydrogen peroxide were injected in the reaction mixture to recover the initial quantities of both reactants and the reaction was continued up to 6 h. The results

Table 1
Effect of the addition of fresh reaction mixture and of the presence of products^a

Description	X_{ST}	$X_{H_2O_2}$	S_{SO}	S_{PADH}	S_{BADH}	S_{DIOL}	S_{others}
Standard test	20.2	40.0	4.2	58.4	13.8	21.2	2.4
Addition of fresh mixture	8.5	15.1	0	53.6	21.8	23.5	1.1
Presence of products							
Initial mixture	27.8	0	10.7	5.5	70.1	7.1	6.6
Final mixture	48.5	56	1.3	32.9	44.4	17.2	4.2
Incremental activity	20.7	56	0	65.6	8.9	25.5	0

^a Reaction conditions: as mentioned in Section 2 with $T_R=60^\circ\text{C}$, and $t_R=3\text{ h}$.

obtained in the second part of this experiment show that the catalytic activity is less than a half compared with the first 3 h of reaction, which demonstrates that the lower reaction rate is not just due to the reactant consumption. The second experiment was carried out using fresh catalyst but changing the usual feed mixture (styrene, hydrogen peroxide and acetone) by other one simulating a final reaction mixture (styrene, hydrogen peroxide, acetone and a certain product distribution). The results of this reaction show the same activity and similar product distribution as that corresponding to the standard fresh mixture, which indicates that equilibrium limitations due to the pres-

ence of the products in the reaction medium must be discarded as the origin of the activity decay.

The spent catalysts obtained in the kinetic experiments were characterised by a number of techniques. Fig. 3 shows the TG analysis of the sample corresponding to the experiment carried out at 50°C . The differential curve of the thermogravimetric analysis indicates that the main weight loss are produced at 42, 130, 200 and 435°C . In order to identify the products occluded in the spent catalysts, TPD–MS analysis of these samples were carried out. Under the assumption that a number of styrene oxidation products (water, oxygen, CO, CO_2 , styrene, phenylacetaldehyde,

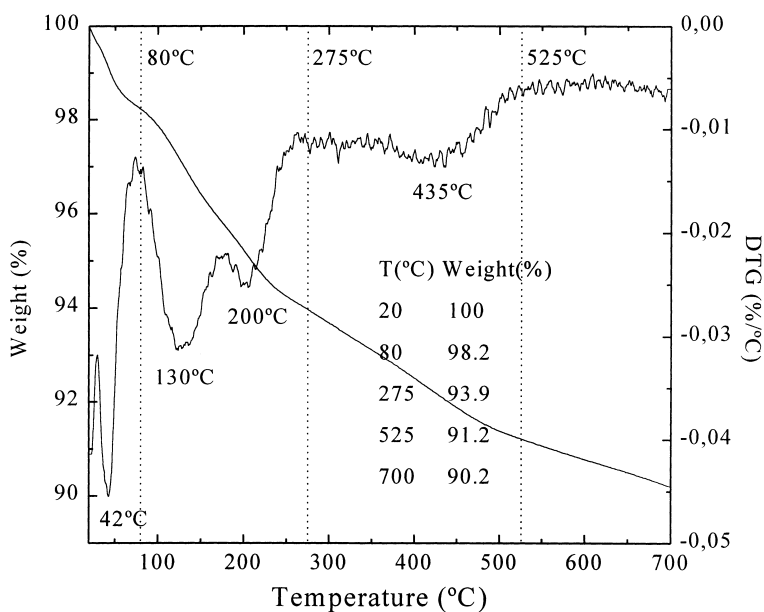


Fig. 3. TG analysis of the spent catalyst obtained at 50°C and 6.5 h.

styrene oxide, benzoic acid, 1-phenyl,1,2-ethanediol, acetophenone, and phenyl-acetic acid) could be desorbed, the following m/z fragments were recorded by quadrupole MS: 4, 18, 28, 32, 44, 90, 91, 103, 104, 105, 106, 107, 119, 120, 122, 130 and 136. Since the TPD–MS analysis starts at 50°C to get rid off signals of the solvent used in the reaction, the peak centred at 42°C in the DTG has not been detected by this technique, although it is probably due to acetone. The next weight loss is produced around 130°C, the products detected by TPD–MS at this temperature being water and styrene. The desorption peak centred at 200°C is due mainly to PADH and lower amounts of BADH. Finally, a significant weight loss is observed at high temperatures around 435°C. TPD–MS detects, at this temperature, the desorption of styrene and a non-identified fragment with $m/z=91$. However, the weight loss produced in this region cannot be assigned to the desorption of styrene, since its presence within the zeolite pores up to 435°C does not seem feasible. In this way, it is hypothesised that the peak at high temperature arises from the thermal decomposition of styrene oligomeric compounds. It is noteworthy that among the different reaction products, neither DIOL

nor styrene oxide has been detected adsorbed on the spent catalysts by TPD–MS analysis, which shows the low affinity of the TS-1 zeolite by the DIOL and the fast isomerisation of styrene oxide.

Fig. 4 illustrates the evolution of both styrene and H_2O_2 conversions with the time at 40°C (Fig. 4a), as well as the TG analysis of the spent catalysts obtained after 6.5 and 24 h (Fig. 4b and c, respectively). Although the variation of the reactant conversions indicates that the reaction rate remains almost constant beyond 5 h, the TG analysis of these two spent catalysts exhibit great differences. Both samples present similar weight loss below 275°C, although the peak maximum shifts from 131 up to 181°C as the reaction time is increased. Both TGA and TPD–MS data show that the proportion of styrene occluded in the spent catalysts decreases, while the amounts of phenylacetaldehyde and benzaldehyde are enhanced with the reaction time. Moreover, the TG peak centred at 425°C increases strongly in the sample obtained after 24 h of reaction, with a proportion around 12 wt.%. Since the maximum adsorption capacity of TS-1 is about 13 wt.%, this result suggests that the styrene oligomers are not really present within the zeolite pores, but

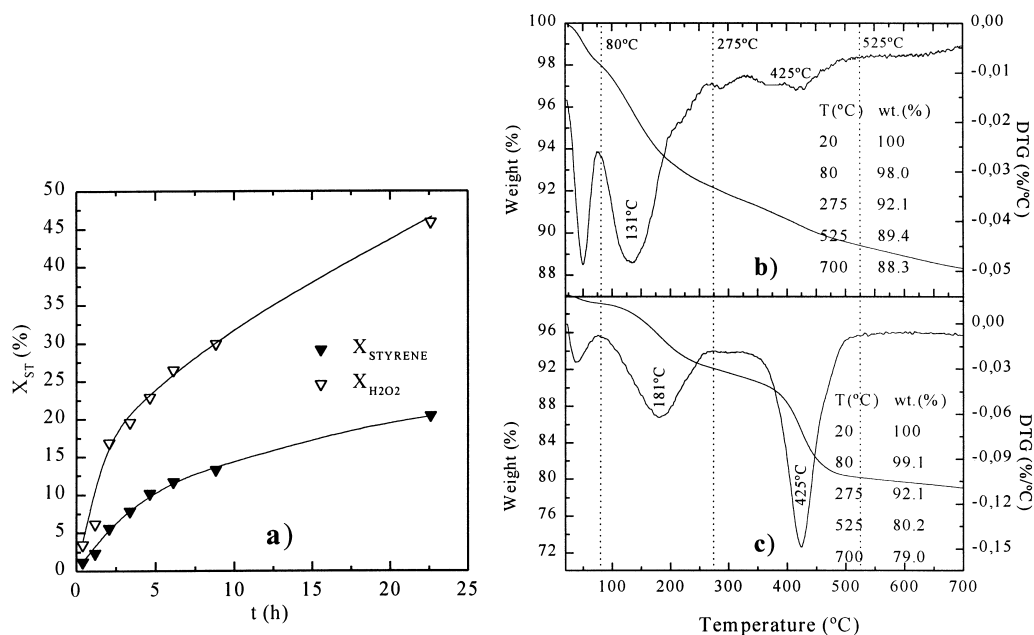


Fig. 4. Styrene and H_2O_2 conversions at (a) 40°C, and TG analysis of the spent catalysts obtained at (b) 6.5 h; (c) 24 h.

Table 2

Weight losses in the TG analysis of the spent catalysts at all temperatures investigated

T (°C)	t (h)	Weight loss (%) at			Total weight loss (%)
		20–80°C	80–275°C	275–525°C	
70	6.5	1.8	3.7	3.0	9.6
60	6.5	1.9	4.5	4.1	11.7
50	6.5	1.8	4.3	2.7	9.8
40	6.5	2.0	5.9	2.7	11.7
40	24	0.9	7.0	11.9	21.0

on the contrary they are formed and precipitated directly from the solution, being probably recovered with the catalyst in the centrifugation step after the reaction.

Table 2 summarises the main weight loss observed by TGA of the spent catalysts for the four kinetic experiments carried out at different temperatures. All the samples present similar DTG curves, although those obtained at 40°C show just a single peak in the range 80–275°C. As the temperature decreases or the reaction time increases, the weight loss produced in this region is enhanced, mainly due to the release

of styrene and aldehydes. This fact suggests that a strong adsorption of styrene, phenylacetaldehyde and benzaldehyde takes place on the Ti sites of the spent catalysts. It is known that the equilibrium of the adsorption phenomenon is favoured at lower temperatures. It is noteworthy that, just taking into account the weight loss corresponding to the TGA peak in the range 80–275°C, almost half of the pore volume of the TS-1 zeolite is occupied by aromatic compounds. This high concentration of products within the zeolite pores leads probably to important diffusion limitations, which may also affect negatively the catalytic activity compared to the fresh TS-1 sample.

Fig. 5a shows the DR UV–Vis spectra as well as the XRF analysis of the spent catalysts, compared to those of the fresh TS-1 zeolite. DR UV–Vis of the fresh sample shows a narrow absorption band at 210–220 nm, which has been assigned in the literature to the Ti species with tetrahedral coordination incorporated into the zeolite framework. Moreover, the absence of absorption in the regions around 275 and 330 nm denotes that hexacoordinated Ti atoms and extra framework TiO_2 are not present in the fresh sample. Therefore, it can be concluded that in the raw

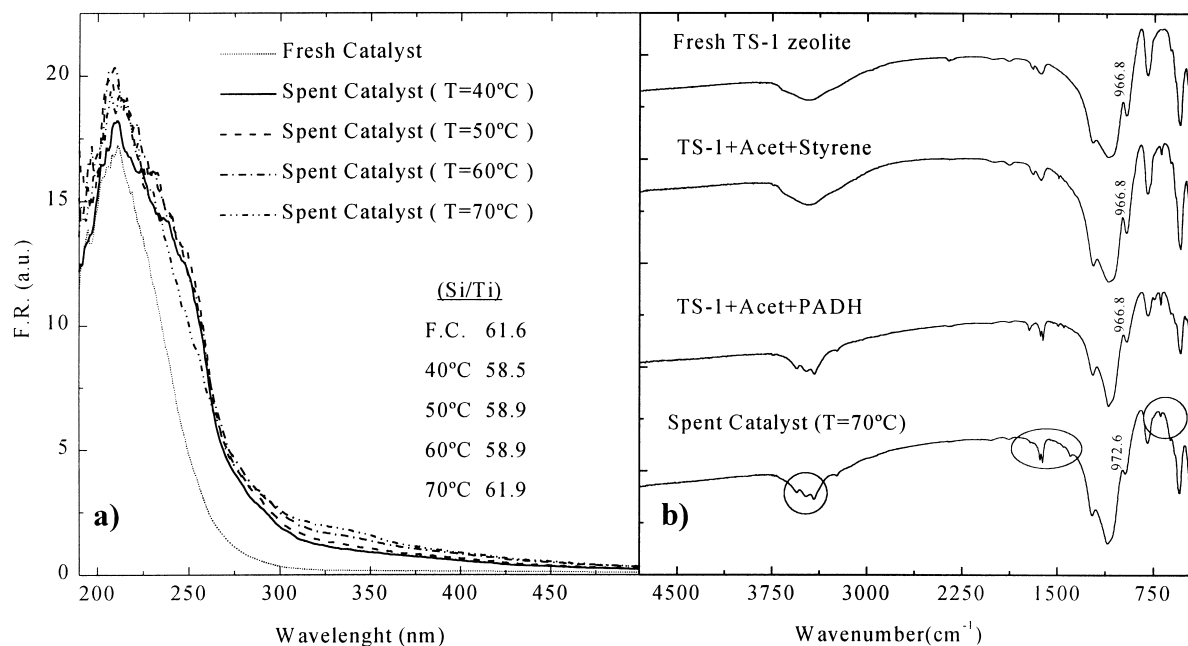


Fig. 5. Characterisation of fresh and spent TS-1 samples: (a) DR UV–Vis; (b) FTIR.

TS-1 catalyst, all the Ti atoms exhibit a tetrahedral environment [6,7]. Although XRF analysis indicates that no Ti species are leached during the reaction, a shift in the DR UV–Vis spectra absorption bands towards higher wavelength is observed in the used samples. It is known that the interaction of different molecules with the Ti atoms in TS-1 zeolite leads to a change in its coordination from tetrahedral to penta- and hexa-coordinated species, which causes the appearance of new UV–Vis bands in the range 230–280 nm [8]. Accordingly, the observed shift towards higher wavelengths in the DR UV–Vis spectra of the spent catalysts can be related to the adsorption of some of the occluded species on the Ti sites. However, since most of the reaction products show also DR UV–Vis absorption bands in the range of 204–350 nm [9], the wider spectra of the spent catalysts could be alternatively caused just by the presence of these products on the zeolite. A comparison of the DR UV–Vis spectra of silicalite-1 and TS-1 zeolites impregnated with the main reaction products with the spectra corresponding to the spent catalysts indicates that the first reason seems to be responsible for the wider absorption bands. Therefore, it can be concluded that a part of the Ti atoms in the spent TS-1 exhibit coordination different from tetrahedral due to the chemisorption of styrene, phenylacetaldehyde and benzaldehyde, which are the main species occluded within the zeolite pores, as detected by TPD–MS.

Fig. 5b shows the FTIR spectra of the spent catalyst obtained at 70°C compared with that of the fresh TS-1 zeolite, as well as those of two samples obtained by impregnation of TS-1 zeolite with acetone+phenylacetaldehyde and acetone+styrene, respectively. Fresh TS-1 zeolite presents a band at 960 cm⁻¹, which is commonly assigned in the literature to the stretching vibration of [SiO₄] units linked to Ti atoms, confirming that the Ti atoms are linked to the zeolite framework [10,11]. The IR bands characteristic of the major products adsorbed in the used TS-1, styrene and phenylacetaldehyde, are clearly observed in the FTIR spectrum of the spent catalyst (marked regions) [12]. Another important difference observed between the FTIR spectra of the spent catalyst and the fresh TS-1 zeolite is the position of the 960 cm⁻¹ band. Whereas in the fresh TS-1 zeolite and the samples impregnated with PADH and styrene

this band appears at 966.8 cm⁻¹, the spent catalyst shows this absorption band at 972.6 cm⁻¹. This result confirms that a change in the Ti coordination takes place during the reaction, which is in agreement with the results obtained from the DR UV–Vis spectra.

4. Conclusions

The reasons of the TS-1 zeolite deactivation during the styrene oxidation with H₂O₂ have been investigated through a series of kinetic experiments in the temperature range 40–70°C, and by characterisation of the spent catalysts by a number of techniques. In all temperatures investigated a strong initial decay of the catalytic activity has been found, the presence of equilibrium limitations of the reaction products and the consumption of the reactants being discarded as its origin. TG and TPD–MS analyses carried out on the solid recovered at the end of the kinetic experiments indicate that two different types of products are desorbed at different temperature ranges. The products coming out around 180–200°C (water, styrene, phenylacetaldehyde and benzaldehyde) are adsorbed within the zeolite pores, whereas the products detected at higher temperatures around 430°C, are generated by the thermal decomposition of styrene oligomeric compounds. These oligomers are formed and precipitated from the solution, being recovered with the spent catalyst in the centrifugation step after the reaction. Low reaction temperatures increase the proportion of the products adsorbed within the zeolite pores, whereas high reaction temperatures increase the formation of oligomeric compounds in the reaction medium. Likewise, higher reaction times favour both types of phenomena. Finally, it can be concluded that although no Ti atoms are extracted from the zeolite during the reaction, a part of them change their coordination to higher than tetrahedral due to a strong adsorption of different species, mainly styrene, phenylacetaldehyde and benzaldehyde. The decline of the TS-1 activity during the first hours of reaction has been assigned to the chemisorption of different aromatic species on the Ti sites, as well to the presence of diffusion limitations arising from the high degree of occupancy of the zeolite pores and intersections.

Acknowledgements

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