



ELSEVIER

Journal of Molecular Catalysis A: Chemical 111 (1996) 167–174

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

# Microwave heating in the TS-1 catalyzed oxyfunctionalisation of *n*-hexane

P.J. Kooyman<sup>\*</sup>, G.C.A. Luijkx, A. Arafat, H. van Bekkum

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Received 8 March 1996; accepted 15 May 1996

## Abstract

Using the zeolite TS-1 catalyzed oxyfunctionalisation of *n*-hexane with aqueous hydrogen peroxide as a model reaction, the use of microwave heating is compared to conventional heating. Using microwave heating, hydrogen peroxide conversion is higher than using conventional heating, although the efficiency of incorporation of oxygen into *n*-hexane is lower. Adsorption measurements using an FT-IR microscope method reveal a synergism of adsorption into the zeolite between *n*-hexane and hydrogen peroxide.

**Keywords:** TS-1; Microwave heating; *n*-Hexane oxyfunctionalisation; Hydrogen peroxide

## 1. Introduction

Recently, domestic microwave ovens have been introduced to chemical laboratories as an alternative heating tool to conventional conductive heating methods [1,2]. Rate enhancement of reactions is the main feature of this technique, and this is mainly due to temperature and pressure effects. However, in some catalytic organic reactions using microwave heating, apart from rate enhancement also increased selectivity or increased catalyst stability have been reported [3].

The microwave region of the electromagnetic spectrum, 300 MHz–300 GHz, lies in between the infrared and radio frequencies. Domestic

microwave ovens generally operate at 2.45 GHz (12.2 cm). Microwave dielectric heating is based on the ability of some liquids and solids to transform electromagnetic energy into heat. This ability is expressed in the dissipation factor,  $\tan \delta$ . The higher  $\tan \delta$ , the better the dissipation of microwave radiation energy. Polar molecules have a high  $\tan \delta$ . Microwave energy is absorbed by molecules with a high  $\tan \delta$  as rotation energy, resulting in a ‘wobbling’ of the molecules, through which the absorbed energy is converted to kinetic energy. The penetration depth of microwave radiation depends on the dissipation factor of the substances to be heated and is a few centimeters.

Reaction vessels that are to be used with microwave heating should be constructed from microwave transparent materials. Metals cannot be used in microwave ovens, because they reflect the microwave radiation.

<sup>\*</sup> Corresponding author. E-mail: patricia.kooyman@stm.tudelft.nl.

Table 1  
Dissipation factors of some common solvents at 3 GHz

Solvent	tan $\delta$	bp (°C), conventional	$T$ easily reached in microwave	Superheating above bp (°C)
Water	0.157 [4]	100	104 [5], 110 [6]	4, 10
Methanol	0.640 [2]	65	84 [5]	19
Ethanol	0.250 [2]	79	103 [5]	24

One thing that has to be kept in mind when using microwave heating is the tendency of liquids to be superheated, although the degree to which a liquid is superheated depends on several factors, like the amount of dissolved gases and impurities, and the roughness of the surface of the container in which the liquid is placed. Table 1 lists some common solvents, their dissipation factors and the temperatures to which they can be superheated easily.

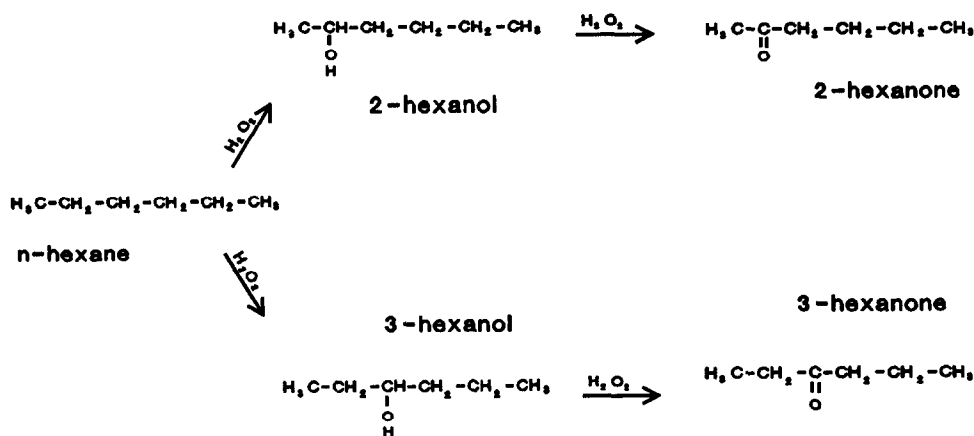
A study on the microwave heating of zeolites indicated that the heating rates of zeolites are dependent on the composition of the zeolite (e.g. the type of charge-balancing counter-ions) [7]. Solvated ions and counter-ions in zeolites 'wobble' to and fro, directly converting the microwave energy to kinetic energy. The kinetic energy thus generated can be passed on to other (non-microwave absorbing) molecules through common interactions, resulting in a rise in temperature of the entire reaction mixture.

In the present paper we report on the use of both microwave and conventional heating in a

heterogeneously catalyzed oxidation. The reaction studied is the oxyfunctionalisation of *n*-hexane using aqueous hydrogen peroxide as the oxidizing agent and TS-1 (titanium-silicalite-1) as the catalyst. The reactants are in the liquid phase; the zeolitic catalyst is a solid-phase material. The product mixture consists of a mixture of 2- and 3-hexanol and 2- and 3-hexanone [8] (see Scheme 1). For this reaction, Huybrechts et al. [8] propose a radical mechanism, whereas Tatsumi et al. [9] propose a concerted mechanism.

## 2. Experimental

Using conventional heating techniques, the oxyfunctionalisation of *n*-hexane is suitably performed in a Teflon-lined stainless steel autoclave, which is placed in a pre-heated metal oven, in which the metal of the oven is in direct contact with the autoclave. When employing microwave heating, an all-Teflon (PTFE) auto-



Scheme 1. The oxyfunctionalisation of *n*-hexane.

Table 2  
Reaction conditions for *n*-hexane oxyfunctionalisation

	Conventional heating	Microwave heating
Autoclave total volume	25 ml	100 ml
Catalyst	20 mg	80 mg
Methanol	10 ml	40 ml
<i>n</i> -hexane (Baker, Z.A.)	1.0 ml (7.68 mmol)	4.0 ml (30.72 mmol)
30% H <sub>2</sub> O <sub>2</sub> (Merck, p.a.)	0.80 ml (7.84 mmol)	3.20 ml (31.36 mmol)
Temperature	100°C	100°C

clave is used. Methanol is used as a solvent. The exact reaction conditions are listed in Table 2.

The microwave equipment employed in this work is a Gerling Moore microwave generator equipped with an S-band WR-284 wave guide, operating in the TE<sub>10</sub> mode (see Scheme 2).

The experimental set-up is similar to that described by Graef et al. [10]. A continuously variable power with a maximum of 2500 W can be applied; the microwave source operates at 2.45 GHz. An all-Teflon (PTFE) autoclave of 2.2 cm inner diameter was used, placed in the wave-guide via a shielded hole of 3 cm inner diameter. The temperature was measured by positioning an earth-connected thermocouple in the liquid phase but outside the microwave cavity.

The catalyst used, Euro-TS-1, was obtained from Dr. A.J.H.P. van der Pol, Eindhoven University of Technology. Euro-TS-1 is the result of the first attempt to synthesize a 'standard' TS-1 catalyst that can be used as a reference sample by anyone studying TS-1. The material was received 'as synthesized'. To remove the template (TPA, tetrapropylammonium), the ma-

terial was calcined in air at 500°C overnight prior to use. The Si/Ti ratio of the TS-1 calcined material was 60 as determined using ICP-AES (inductively coupled plasma - atomic emission spectroscopy) analysis. The catalyst average particle size is 0.15 μm.

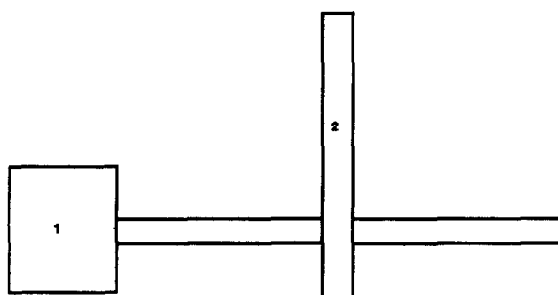
The suspension of the catalyst in the otherwise homogeneous reaction mixture is stirred. For both conventional and microwave heating blank reactions, without the addition of catalyst, were performed. Products are determined using GC analysis, for which toluene is used as GC standard, added after reaction; H<sub>2</sub>O<sub>2</sub> conversion is monitored using iodometric titration.

Large crystals of TS-1 (30 μm, Si/Ti ratio 70) obtained through direct synthesis using F<sup>-</sup> instead of OH<sup>-</sup> as the mineralizing agent [11], were used in adsorption experiments. These experiments were performed by refluxing the zeolite in the liquid (or solution) for a few minutes, cooling to room temperature and evaporating excess liquid at ambient conditions. Selected crystals were placed under the IR microscope on a thin flake of KCl, and adsorbed species were studied by measuring the IR absorption spectrum in transmission mode. The IR equipment used was a Bruker IFS 66 FT-IR spectrophotometer. Spectra were calculated from 500 or 1000 scans, with a resolution better than 8 cm<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Catalytic experiments

As can be seen from Tables 3 and 4 and Fig. 1, the hydrogen peroxide conversion rate is much higher when using microwave heating



Scheme 2. Schematic drawing of the microwave set-up: (1) variable power microwave generator; (2) all-Teflon autoclave.

Table 3  
(Euro-) TS-1 catalyzed *n*-hexane oxyfunctionalisation using microwave heating

Time (h)	H <sub>2</sub> O <sub>2</sub> conv.	H <sub>2</sub> O <sub>2</sub> conv. <sup>a</sup>	Yield 2-ol <sup>b</sup>	Yield 3-ol <sup>b</sup>	Yield 2-one <sup>b</sup>	Yield 3-one <sup>b</sup>	H <sub>2</sub> O <sub>2</sub> eff. <sup>c</sup>
b <sup>d</sup> 3	52%	16.31	0.07	0.03	0.06	0.06	2.1%
0.5	12%	3.76	0.94	0.67	0	0	42.8%
1	34%	10.66	2.04	1.04	0.54	0.01	39.2%
1.5	41%	12.86	2.82	1.43	0.44	0.10	41.4%
3	92%	28.85	3.66	2.05	2.15	0.38	37.3%

For reaction conditions see Table 2.

<sup>a</sup> mmol of H<sub>2</sub>O<sub>2</sub> consumed.

<sup>b</sup> Yield = mmol of product formed.

<sup>c</sup> Efficiency = (mmol of -ols formed + 2 \* mmol of -ones formed / (mmol of H<sub>2</sub>O<sub>2</sub> converted)) \* 100%.

<sup>d</sup> No catalyst added.

than when using conventional heating. However, when using conventional heating, the efficiency of the reaction based on hydrogen peroxide conversion is higher than when using microwave heating. Apparently, more hydrogen peroxide is decomposed when using microwave heating.

The TS-1, a zeolite containing only 4-valent T-atoms, does not contain a substantial amount of OH-groups, and is hydrophobic. Thus, it should not absorb microwave radiation, which was verified by subjecting it to 400 W microwave radiation for 25 min, upon which its temperature did not rise. This means that in the catalytic experiments the reaction mixture is heated through absorption of microwave radiation by the solvent (methanol and some water from the hydrogen peroxide solution), the hydrogen peroxide and the products in the bulk liquid and in the adsorbed phase.

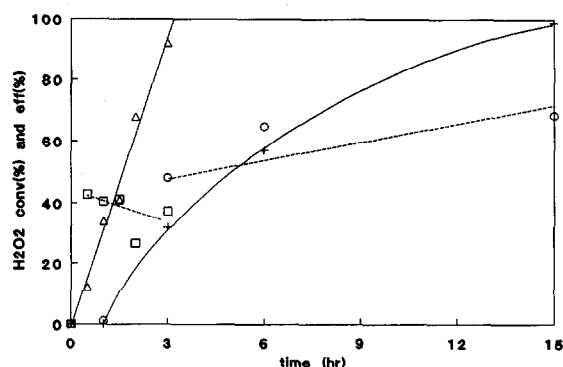


Fig. 1. H<sub>2</sub>O<sub>2</sub> conversion and efficiency in *n*-hexane oxidation with aqueous hydrogen peroxide and TS-1 using conventional (+ = conv.; O = eff.) and microwave ( $\Delta$  = conv.;  $\square$  = eff.) heating techniques.

The blank experiment (i.e., without catalyst) using conventional heating does not give any hydrogen peroxide conversion, whereas the blank experiment using microwave radiation does give significant hydrogen peroxide conver-

Table 4  
(Euro-) TS-1 catalyzed *n*-hexane oxyfunctionalisation using conventional heating

Time (h)	H <sub>2</sub> O <sub>2</sub> conv.	H <sub>2</sub> O <sub>2</sub> conv. <sup>a</sup>	Yield 2-ol <sup>b</sup>	Yield 3-ol <sup>b</sup>	Yield 2-one <sup>b</sup>	Yield 3-one <sup>b</sup>	H <sub>2</sub> O <sub>2</sub> eff. <sup>c</sup>
b <sup>d</sup> 24	0%	0	0	0	0	0	0
1	0%	0	trace	trace	0	0	< 1%
3	32%	2.51	0.63	0.36	0.09	0.02	48.2%
6	57%	4.47	1.14	0.60	0.51	0.07	64.9%
15	99%	7.76	1.34	0.88	1.37	0.18	68.6%

For reaction conditions see Table 2.

<sup>a</sup> mmol of H<sub>2</sub>O<sub>2</sub> consumed.

<sup>b</sup> Yield = mmol of product formed.

<sup>c</sup> Efficiency = (mmol of -ols formed + 2 \* mmol of -ones formed / (mmol of H<sub>2</sub>O<sub>2</sub> converted)) \* 100%.

<sup>d</sup> No catalyst added.

Table 5  
Difference in absolute yields between microwave and conventional heating

Time (h)	Yield 2-ol <sup>a</sup>	Yield 3-ol <sup>a</sup>	Yield 2-one <sup>a</sup>	Yield 3-one <sup>a</sup>
1	0.51	0.26	0.14	0.003
3	0.29	0.15	0.45	0.08

<sup>a</sup> mmol of product formed in microwave heated reaction –  
4 \* mmol of products formed in conventionally heated reaction.

sion (although only small amounts of products). Although some would readily ascribe this difference to a ‘microwave effect’ related to direct activation of the hydrogen peroxide, this is not very feasible. As the activation energy for dissociation of the O–O bond in a free molecule of H<sub>2</sub>O<sub>2</sub> is  $2.4 \times 10^{-19}$  J, and the energy of a photon of microwave radiation at 2.45 GHz is  $1.623 \times 10^{-24}$  J, the direct activation of hydrogen peroxide by the microwave radiation employed is improbable. On the other hand, stirring may still not exclude the presence of ‘hot spots’. Another possibility is that part of the hydrogen peroxide is decomposed on the thermocouple, as hydrogen peroxide can be decomposed on most metals. However, an experiment using silicalite-1 as the ‘catalyst’ does not give any products, nor appreciable hydrogen peroxide conversion (about 5%). One is inclined to think that silicalite-1 somehow stabilizes the hydrogen peroxide, or that it prevents ‘hot spots’

by acting as an efficient boiling stone. Adsorption measurements (vide supra) on the TS-1 show that hydrogen peroxide is indeed adsorbed in a hydrophobic zeolite. When TS-1 is present, a substantially larger part of the converted hydrogen peroxide is used to oxidize the *n*-hexane.

Comparing the absolute yields of products between the microwave and conventionally heated TS-1 catalyzed reaction (listed in Table 5) at the same reaction time, the microwave heated reaction gives higher absolute amounts of products. However, as also the hydrogen peroxide conversion is much higher in the microwave heated reaction, the efficiency of the microwave heated reaction is substantially lower than the efficiency of the conventionally heated reaction.

Using conventional heating, an induction period of about 1 h is observed, which would seem longer than the time needed for the reaction mixture to reach the reaction temperature of 100°C. Although Clerici [12] claims that the oxyfunctionalisation of *n*-alkanes can be performed at 55°C, our own experiments indicate that reaction times of three or more days at that temperature are necessary to obtain detectable amounts of products. In our hands, the reaction does not proceed at temperatures much lower than 100°C.

Table 6 gives the regioselectivity and the ratio of 2- to 3-oxygenated products found for

Table 6  
Regioselectivity in (Euro-) TS-1 catalyzed *n*-hexane oxyfunctionalisation

Time (h)	Heating <sup>a</sup>	H <sub>2</sub> O <sub>2</sub> conv.	Total 2-prod. <sup>b</sup>	Total 3-prod. <sup>b</sup>	Ratio 2/3 prod. <sup>c</sup>
b <sup>d</sup> 3	mw	52%	0.13	0.09	1.44
b <sup>d</sup> 24	conv.	0%	0	0	—
0.5	mw	12%	0.94	0.67	1.40
1	mw	34%	2.58	1.05	2.46
1.5	mw	41%	3.26	1.53	2.13
3	mw	92%	5.81	2.43	2.39
3	conv.	32%	0.72	0.38	1.89
6	conv.	57%	1.65	0.67	2.46
15	conv.	99%	2.71	1.06	2.56

<sup>a</sup> mw = microwave; conv. = conventional.

<sup>b</sup> mmol of -ol formed + mmol of -one formed.

<sup>c</sup> mmol of 2-products formed/mmol of 3-products formed.

<sup>d</sup> No catalyst added.

the catalytic reactions. Although the statistical ratio of 2/3 products is 4/4 (= 1.0), the 2/3 substitution ratio is expected to be 0.91 [13] if the oxyfunctionalisation reaction proceeds solely through an HO $\cdot$  radical mechanism. The ratio found for the blank reaction using microwave heating is 1.44, and we may assume that in that run essentially only reaction through free HO $\cdot$  radicals occurs. Although hydrogen peroxide conversion is over 50%, only small amounts of products are formed in the blank reaction using microwave heating. When TS-1 is added, not only does the total product yield increase sharply, but also the 2/3 product ratio increases, indicating that the hydrogen peroxide is not (only) activated through free radical formation, but (also) in interaction with the catalyst.

If we compare the 2/3 product ratios obtained when using microwave heating to those obtained using conventional heating, we see that generally this ratio is lower for microwave heating, indicating a larger contribution of the free radical mechanism as compared to conventional heating.

### 3.2. Adsorption measurements

In order to get an idea of the adsorbed mixture during catalytic oxidation experiments,

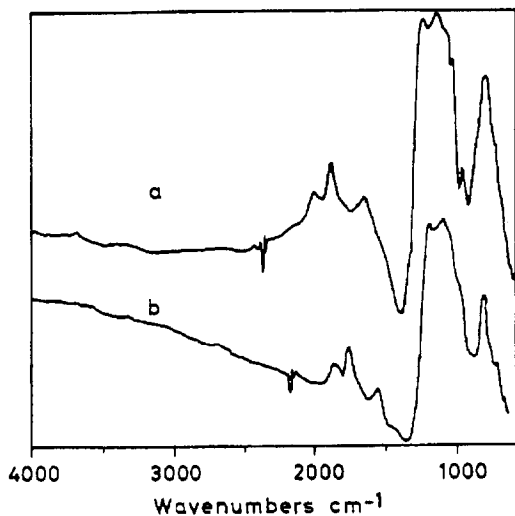


Fig. 2. IR spectra of (a) TS-1-F, (b) TS-1-F refluxed in methanol.

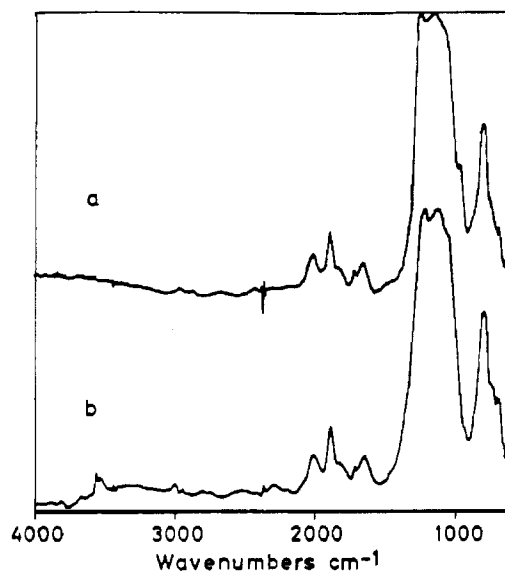


Fig. 3. IR spectra of TS-1-F refluxed in (a) water, (b) 30% H<sub>2</sub>O<sub>2</sub>.

some adsorption experiments were undertaken. These experiments were performed using the large crystals of TS-1 (crystal size 30  $\mu$ m), because the crystals of Euro-TS-1 are too small

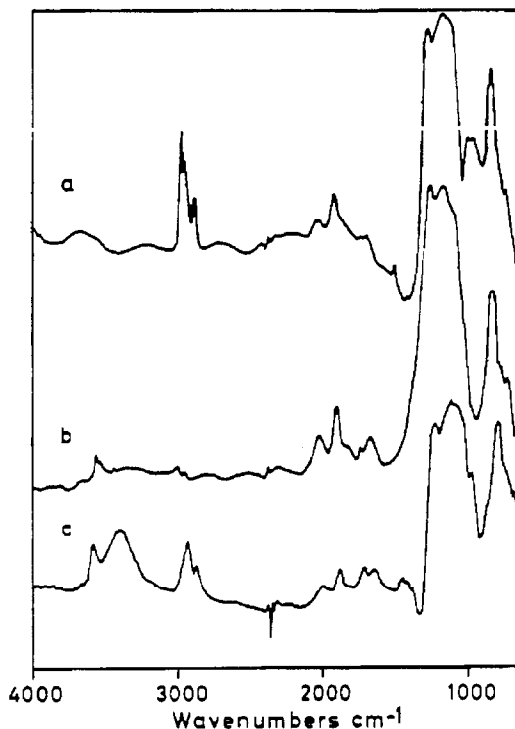


Fig. 4. IR spectra of TS-1-F refluxed in (a) *n*-hexane, (b) 30% H<sub>2</sub>O<sub>2</sub>, (c) *n*-hexane oxyfunctionalisation reaction mixture.

(0.15  $\mu\text{m}$ ) to use them in the IR microscope set-up. This TS-1 is expected to be slightly more hydrophobic than Euro-TS-1.

Fig. 2 shows the IR spectra of TS-1 and of TS-1 refluxed in methanol. These spectra show that methanol is not adsorbed in TS-1. TS-1 is probably too hydrophobic to adsorb methanol.

The IR spectra of TS-1 refluxed in demineralized water and in 30% aqueous hydrogen peroxide are shown in Fig. 3. As expected, water is not adsorbed in the hydrophobic TS-1. However, hydrogen peroxide is adsorbed to some extent, indicating it to be less polar than water or methanol.

In Fig. 4 the spectra of TS-1 refluxed in *n*-hexane, 30% aqueous hydrogen peroxide and in the *n*-hexane oxyfunctionalisation reaction mixture are shown. The non-polar *n*-hexane is easily adsorbed in TS-1, as is to be expected.

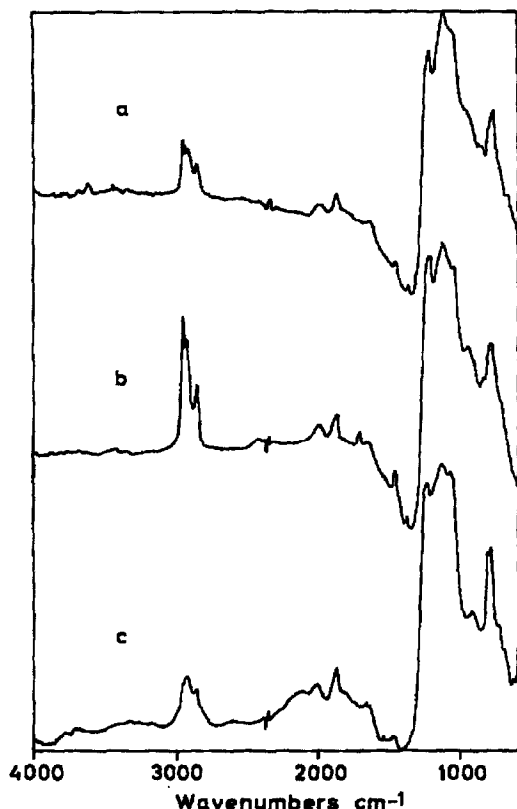


Fig. 5. IR spectra of TS-1-F refluxed in (a) 2-hexanol, (b) *n*-hexane + 30%  $\text{H}_2\text{O}_2$ , (c) *n*-hexane + methanol.

If we study the IR spectrum of TS-1 refluxed in the reaction mixture, we see that molecules containing hydroxyl groups now are adsorbed in TS-1. This may be due to a synergism in adsorption between *n*-hexane (which is also adsorbed from the reaction mixture) and hydrogen peroxide. If *n*-hexane and hydrogen peroxide are adsorbed in TS-1 simultaneously, then reaction between the two should be enhanced, as is indeed found in the catalytic experiments. However, if we study the IR spectra of TS-1 refluxed in 2-hexanol (Fig. 5a), practically no absorption in the –OH region is observed. The same is valid for TS-1 refluxed in a mixture of *n*-hexane and 30% hydrogen peroxide (Fig. 5b) and in a mixture of *n*-hexane and methanol (Fig. 5c). Thus, cautiously our conclusion is that all the components of the reaction mixture are necessary to obtain the synergism in adsorption of *n*-hexane and hydrogen peroxide.

#### 4. Conclusions

The reaction rate of the oxyfunctionalisation of *n*-hexane with hydrogen peroxide using TS-1 as a catalyst can be greatly enhanced by using microwave heating, albeit at a substantially lower reaction efficiency. IR data of adsorbed species on TS-1 synthesized in a fluoride medium show that only in the case of contacting the TS-1 with the total oxyfunctionalisation reaction mixture a synergism of adsorption is found between *n*-hexane and hydrogen peroxide. With the 2/3-product selectivity data available, no definite statement can be made as to which of the two oxygenation reaction mechanisms proposed in literature is the most likely mechanism to operate in reality.

#### Acknowledgements

The authors would like to thank Dr. A.J.M. de Man and Dr. J.C. Jansen for valuable discussions.

**References**

- [1] R.N. Gedye, F.E. Smith and K.C. Westaway, *Can. J. Chem.* 66 (1988) 17.
- [2] D.M.P. Mingos and D.R. Baghurst, *Chem. Soc. Rev.* 20 (1991) 1.
- [3] K. Smith, ed., *Solid supports and catalysts in organic synthesis* (Ellis Horwood PTR Prentice Hall, New York, 1992).
- [4] J.R. White, *Trans. IMPI* 1 (1973) 40.
- [5] D.R. Baghurst and D.M.P. Mingos, *J. Chem. Soc. Chem. Commun.* (1992) 974.
- [6] J. Walker, *Sci. Am.* 256 (1987) 98.
- [7] B.I. Whittington and N.B. Milestone, *Zeolites* 12 (1992) 815.
- [8] D.R.C. Huybrechts, L. de Bruyker and P.A. Jacobs, *Nature* 345 (1990) 146.
- [9] T. Tatsumi, M. Nakamura and H. Tominaga, *Catal. Soc. Jpn.* 33 (1991) 444.
- [10] M. Graef, G.G. Allan and B.B. Krieger, *Prepr. Pap. Div. Petr. Chem. Am. Chem. Soc.* 24 (1979) 432.
- [11] P.J. Kooyman, J.C. Jansen and H. van Bekkum, in: *Proc. 9th International Zeolite Conference*, ed. R. van Ballmoos, J.B. Higgins and M.M.J. Treacy, Vol. 1 (Butterworth-Heinemann, Stoneham, MA, 1993) p. 505.
- [12] M.G. Clerici, *Appl. Catal.* 68 (1991) 98.
- [13] A.C. Besemer, Ph.D. thesis, Delft University of Technology, 1993.