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Hydroxylation of phenol with hydrogen peroxide on EUROTS-1 catalyst

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Abstract

The catalytic performance of a standard titanium molecular sieve catalyst, EUROTS-1, has been evaluated at four European universities. The hydroxylation of phenol into catechol and hydroquinone with aqueous H₂O₂ solution was selected as catalytic test reaction. The use of standard EUROTS-1 catalyst permitted to establish a reproducible standard reaction procedure. The calcination conditions of the catalyst, the use of internal standards, and the nature and the amount of the solvent added to the reaction mixture were found to be major factors determining phenol conversion, product selectivity and hydrogen peroxide product yield.

Keywords: 1,4-benzoquinone; catechol; EUROTS-1; hydrogen peroxide; hydroquinone; hydroxylation; phenol; titanium silicalite-1; TS-1

INTRODUCTION

Within the frame of the European Association of Catalysis (Eurocat), collaborative research is performed in the area of standardisation of heterogeneous catalysts. Previous research activities have focused on a standard Pt/silica catalyst, EUROPT-1 [1-6] and Ni/silica catalyst, EURONI-1 [7-9]. In

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the area of molecular sieves, a study has been initiated on titanium silicalite-1 (TS-1) as a catalyst for the partial oxidation of organic substrates.

The selective partial oxidation of organic substrates with hydrogen peroxide on TS-1 represents new catalytic chemistry, which is at the basis of important innovations in partial oxidation technology [10]. The growing interest of the scientific community in partial oxidation with titanium molecular sieves is manifested in the more than 100 scientific publications and patents [11] that have appeared since the invention of TS-1, in 1983 [12].

The aim of the study was to develop a standard methodology for the catalytic evaluation of titanium molecular sieves, and to develop a standard catalyst. The synthesis of the first standard EUROTTS-1 catalyst, and its characterisation and catalytic testing in four European university laboratories is reported in this paper.

Selection of the catalytic test reaction

Reactions catalyzed by TS-1 that received most attention in literature are the oxidation of alkanes [13,14], the epoxidation of alkenes [15] and the hydroxylation of aromatics [16]. The selection of a suitable catalytic test reaction for the evaluation of TS-1 samples was based on the following criteria: (1) the type of reactor must be generally available; (2) the reaction procedures must be simple and reproducible and (3) the test must be sensitive to minor variations in catalyst properties.

Disadvantages related to propene epoxidation are the high-pressure equipment to be used and the high reaction exothermicity. In the oxidation of heavier alkenes or alkanes complications arise due to the immiscibility of the aqueous hydrogen peroxide solution and the organic reactant [17]. The hydroxylation of phenol into hydroquinone and catechol does not suffer from these disadvantages and can be performed at atmospheric pressure. Moreover, the hydroxylation of phenol is extremely sensitive to the quality of the catalyst [18].

From literature [19-22], it appears that the product selectivity and yield in the phenol hydroxylation on TS-1 can be very sensitive to many reaction parameters, such as the amount of catalyst, reaction time, reaction temperature and nature of the solvent. Phenol hydroxylation on TS-1 seems to be a combination of intracrystalline catalysis and catalysis at the external crystal surfaces [19], the latter being devoid of any molecular shape-selectivity and favouring the formation of catechol and tar. The shape-selective intracrystalline space favours hydroquinone formation. At low conversion, overoxidation of hydroquinone into 1,4-benzoquinone is important [20]. 1,4-Benzoquinone formation is enhanced when hydrogen peroxide is added at once instead of gradually. For the hydroxylation of phenol on TS-1, acetone and methanol have been recognized as the better solvents [21,22]. In contrast to methanol, acetone seems to be able to remove the tarry products from the external surface

of the catalyst crystals. Consequently, the use of acetone as solvent leads to higher selectivities for catechol compared to hydroquinone.

EXPERIMENTAL

Synthesis and characterisation of EUROTS-1

The synthesis of 150 g of EUROTS-1 was based on the recipe, described in example 1 of the original patent [12]. A synthesis hydrogel is made from the appropriate amounts of tetraethyl orthosilicate (TEOS) from Merck (Selectipur > 99.5), tetraethyl orthotitanate (TEOT) from Merck (For Synthesis), tetrapropylammonium hydroxide (TPAOH) from Alpha, 40% in water, and water according to the following compositional molar relations: $\text{SiO}_2/\text{TiO}_2=35$; $\text{OH}^-/\text{SiO}_2=0.36$; $\text{H}_2\text{O}/\text{SiO}_2=28.2$. TEOT was added dropwise into TEOS under stirring in a teflon beaker. The beaker was covered and flushed with nitrogen gas to prevent carbon dioxide contamination from the ambient air. The temperature was raised to 35°C and the two reagents mixed for 30 min. Subsequently, the TEOS-TEOT mixture was cooled to 0°C. TPAOH cooled at 0°C was added dropwise under stirring. When a white precipitate formed, further addition of TPAOH was interrupted until it disappeared. A clear solution was obtained, which was heated to 80–90°C in 1 h. The solution was stirred during 4 h at this temperature. Water was added to restore the initial volume. The crystallization was performed under stirring (120 rpm) in a two-liter autoclave, at a temperature of 175°C. The crystallization time was 4 days, instead of the 10 days mentioned in the original patent [12].

The Si/Ti atomic ratio of EUROTS-1 was determined at TUE and ETH by AAS, after dissolution of the sample with H_2SO_4 and HF. The Si/Ti atomic ratio of EUROTS-1 has a value of 34, reflecting the gel composition.

The calcination conditions applied in the different laboratories are given in Table 1.

X-ray powder diffraction was performed at TUE on a Philips PW 7200 instrument. EUROTS-1 is phase pure. Uncalcined and TUE-calcined EUROTS-1 have orthorhombic symmetry. Unit cell parameters for the as-synthesized sample are $a=2.003 \pm 0.003$ nm; $b=1.993 \pm 0.006$ nm and $c=1.339 \pm 0.003$ nm; for the TUE-calcined sample $a=2.000 \pm 0.004$; $b=1.993 \pm 0.004$; $c=1.338 \pm 0.005$.

The BET specific surface area of TUE-calcined EUROTS-1 was determined at TUE on a Carlo Erba Strumentazione Sorptomatic 1900. The BET surface area of TUE-calcined EUROTS-1 is 435 m²/g.

Infrared spectra of as-synthesized EUROTS-1 and EUROTS-1 calcined according to procedure B of Table 1 were recorded at KUL on a Nicolet 730 Fourier transform IR (FT-IR) instrument (Fig. 1). The IR spectrum of calcined EUROTS-1 shows a band at ca. 960 cm⁻¹, characteristic of the catalyt-

TABLE 1

Calcination conditions for EUROTS-1

Research team	KUL		TUE	ETH	TUD	
	(A)	(B)	(C)	(D)	(E)	(F)
Type of furnace	Muffle	Tubular	Tubular	Muffle	Muffle	Muffle
Atmosphere	Air	Oxygen	Air	Air	Air	Air
	Static	Flow	Flow	Static	Static	Static
Heating rate ($^{\circ}\text{C}/\text{min}$)	5	5	5	5	1	1
Maximum temperature ($^{\circ}\text{C}$)	550	550	550	550	400	500
Time (h) at max. temperature	3	3	3	3	16	16

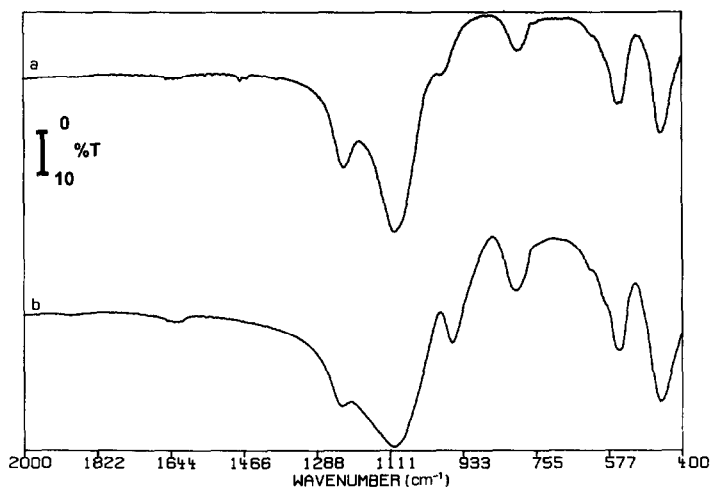


Fig. 1. IR transmission spectrum of as-synthesized EUROTS-1 (a) and EUROTS-1 calcined according to procedure B (b).

ically active site in TS-1 [12,18]. This band is much weaker in the as-synthesized sample. There is a debate on the nature of the titanium species giving rise to this IR band. Framework titanium [23,24], titanyl groups [10,18,25] or monomeric and dimeric edge-sharing titanium tetrahedra [26] have been proposed.

A diffuse reflectance spectroscopy (DRS) UV spectrum of EUROTS-1 calcined according to procedure B of Table 1 was recorded at KUL with a Cary 5 instrument (Fig. 2). The absorption below $35\,000\text{ cm}^{-1}$ is due to a charge transfer between Ti^{IV} and lattice oxygen in zeolitic Ti-O [23-24]. Charge transfer bands at lower wavenumbers typical for bulk anatase ($27\,000\text{--}28\,000$

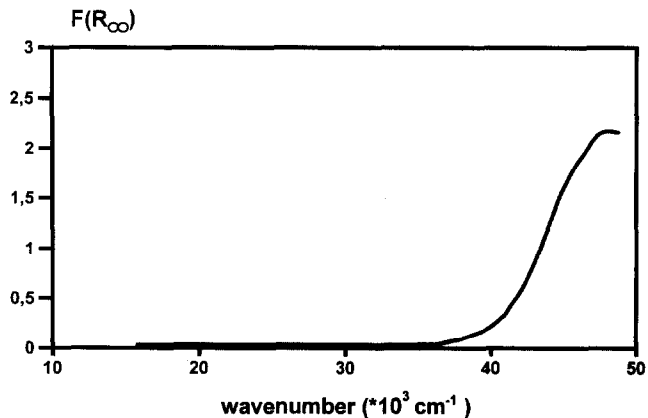


Fig. 2. DRS spectrum of EUROTS-1 calcined according to procedure B.

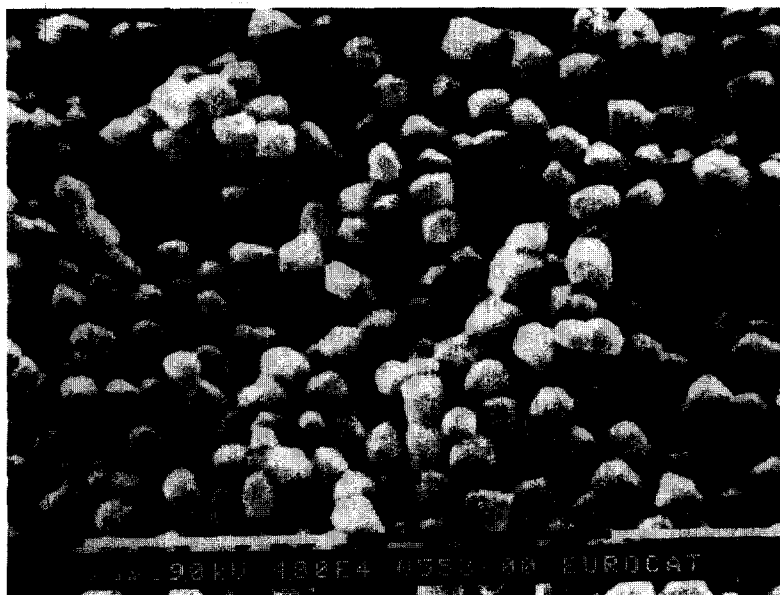


Fig. 3. SEM photograph of EUROTS-1.

cm^{-1}) [27] and occluded TiO_2 (approximately $30\,500\text{ cm}^{-1}$) [11,27] are absent.

The crystal size and morphology of EUROTS-1 were determined at TUE with a Jeol-840 A scanning electron microscope. EUROTS-1 crystallizes as small rounded cubes of ca. $0.15\ \mu\text{m}$ (Fig. 3). The crystal size distribution is very homogeneous (Fig. 4).



Fig. 4. SEM photograph of EUROTS-1.

Catalytic test conditions

The hydroxylation of phenol has been performed in glass vessels, equipped with a reflux condenser and a mechanic or magnetic stirrer. Analytical grade reactants were used in all experiments. Catalyst, phenol, solvent and water are introduced in the reactor, in the order mentioned. The mixture is then heated to reflux temperature. Subsequently, the reaction is started by adding gradually the aqueous hydrogen peroxide solution using a metering pump, while the reactor content is continuously stirred. The reaction is stopped by cooling of the reactor to room temperature. Further details on the reaction conditions are listed in Table 2.

The analysis of the organic reaction products is performed either with gas chromatography (GC) or high-performance liquid chromatography (HPLC) (Table 3). The H_2O_2 concentration is determined with iodometric titration. The amount of tar was determined on product samples from which the catalyst was removed by filtration and the volatile products by evaporation in vacuo.

The conversions (X), selectivities (S) and yields (Y) obtained in the phenol hydroxylation experiments are calculated in the following way:

$$X_{\text{H}_2\text{O}_2}(\%) = 100 \cdot ([\text{H}_2\text{O}_2]_i - [\text{H}_2\text{O}_2]_f) / [\text{H}_2\text{O}_2]_i$$

$$X_{\text{phenol}}(\%) = 100 \cdot ([\text{phenol}]_i - [\text{phenol}]_f) / [\text{phenol}]_i$$

TABLE 2

Reaction conditions for the hydroxylation of phenol on calcined EUROT-S-1

Research team:	KUL				TUE	ETH		TUD	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
<i>Reaction mixture</i>									
Catalyst (g)	0.72	0.36	0.36	0.5	1.00	1.00	1.00	0.10	0.10
Phenol (g)	20.72	8.25	8.25	4.14	20.74	20.88	20.88	10.00	10.00
H ₂ O ₂ solution (g)	5.46 ^a	2.45 ^a	2.45 ^a	1.10 ^a	5.24 ^b	5.55 ^a	5.55 ^a	5.55 ^c	5.55 ^c
PFBA ^d (g)	-	-	-	-	-	1.00	-	1.00	1.00
Methanol (g)	-	1.58	1.58	18.0	-	-	-	32.00	32.00
Acetone (g)	3.79	-	-	-	3.85	2.88	2.88	-	-
Water (g)	3.00	1.22	1.22	-	5.04	5.00	5.00	-	-
Catalyst calcination ^e	(B)	(A)	(B)	(A)	(C)	(D)	(D)	(F)	(E)
Reaction temperature (°C)	100	100	100	69	100	100	100	80	80
H ₂ O ₂ addition rate (min)	45	45	45	45	45	45	45	10	10

^a35 wt.-% in water.^b36 wt.-% in water.^c30 wt.-% in water.^dPentafluorobenzoic acid used as internal standard.^eSpecified in Table 1.

TABLE 3

Analysis of organic reaction products

Research team	Technique	Column	Eluent	Detector
KUL	GC	CP-Sil-5 (chrompack)	-	F.I.D.
TUE	HPLC	RP, C18 column	90% water 10% methanol	UV
ETH	HPLC	RP, C18 column	76.7% water 12.5% methanol 8.3% acetonitrile 2.5% tetrahydrofuran	UV
TUD	HPLC	RP, C18 column	85.5% water 13.5% methanol 1% tetrahydrofuran 0.02% trifluoro acetic acid	UV

$$S_{\text{hydroxylation,phenol}} (\%) = 100 \cdot ([\text{catechol}]_f + [\text{hydroquinone}]_f + [1,4\text{-benzoquinone}]_f) / ([\text{phenol}]_i - [\text{phenol}]_f)$$

$$S_{\text{hydroxylation,H}_2\text{O}_2} (\%) = 100 \cdot ([\text{catechol}]_f + [\text{hydroquinone}]_f + [1,4\text{-benzoquinone}]_f) / ([\text{H}_2\text{O}_2]_i - [\text{H}_2\text{O}_2]_f)$$

$$S_{\text{tar}} (\text{wt.}\%) = 100 \cdot W_{\text{tar}} / (W_{\text{catechol}} + W_{\text{hydroquinone}} + W_{1,4\text{-benzoquinone}} + W_{\text{tar}})$$

$$o/p\text{-selectivity} = [\text{catechol}]_f / ([\text{hydroquinone}]_f + [1,4\text{-benzoquinone}]_f)$$

$$Y_{\text{hydroxylation,phenol}} (\%) = X_{\text{phenol}} \cdot S_{\text{hydroxylation,phenol}} / 100$$

$$Y_{\text{hydroxylation,H}_2\text{O}_2} (\%) = X_{\text{H}_2\text{O}_2} \cdot S_{\text{hydroxylation,H}_2\text{O}_2} / 100$$

in which all concentrations are expressed on a mole basis. The subscripts i and f stand for initial and final, respectively.

RESULTS AND DISCUSSION

Phenol hydroxylation in acetone

In the phenol hydroxylation experiments 1, 5 and 7 (Table 4), acetone was used as solvent. The reaction conditions were similar. The main differences were the smaller amount of catalyst and the longer reaction time in Exp. 1, the smaller amount of acetone in Exp. 7 and the smaller amount of water in Exp.

TABLE 4

Phenol hydroxylation on EUROTTS-1 in acetone (reaction conditions of Table 2)

Exp.	1	5	7	
Reaction time (min)	75	60	60	150
$X_{\text{phenol}} (\%)$	27	27	-	-
$X_{\text{H}_2\text{O}_2} (\%)$	100	100	80	100
$S_{\text{hydroxylation,phenol}} (\%)$	91	73	-	-
$S_{\text{hydroxylation,H}_2\text{O}_2} (\%)$	82	78	87	75
$S_{\text{tar}} (\text{wt.}\%)$	14	20	-	-
$Y_{\text{hydroxylation,phenol}} (\%)$	25	20	16	20
$Y_{\text{hydroxylation,H}_2\text{O}_2} (\%)$	82	78	70	75
<i>Product distribution (mol.-%):</i>				
Catechol	49	51	56	53
Hydroquinone	50	49	40	45
1,4-Benzoquinone	1	0	4	1
<i>o/p</i> ratio	1.0	1.0	1.3	1.1

1. A good agreement between the results obtained at KUL (Exp. 1) and TUE (Exp. 5) was found. In both experiments, the H_2O_2 was completely converted, while the phenol conversion was 27%. This phenol conversion corresponds to the stoichiometric amount that can be hydroxylated with the available H_2O_2 . The hydroxylation selectivity of H_2O_2 was also comparable (82% in Exp. 1; 78% in Exp. 5). However, the hydroxylation selectivity of phenol was significantly higher in Exp. 1 (91%) compared to Exp. 5 (73%). This difference in hydroxylation selectivity of phenol is reflected in the formation of tar, the tar selectivity being higher in Exp. 5 (20%) compared to Exp. 1 (14%). The lower tar selectivity in Exp. 1 could be related to the smaller amount of catalyst used.

The distribution of the hydroxylated products obtained in Exps. 1 and 5 is very similar. In Exp. 1, a trace amount of 1,4-benzoquinone was detected in the reaction products. This compound originates from oxidation of hydroquinone. The *o/p* ratio in the hydroxylated products is close to unity.

Although the reaction conditions used in Exp. 7 at ETH were very similar to the ones used at TUE (Exp. 5), differences in conversion and selectivities were found. In Exp. 7, after 60 min the H_2O_2 conversion was only 80%. The hydroxylation selectivity of H_2O_2 decreased from 87% at 80% H_2O_2 conversion to 75% at 100% H_2O_2 conversion. This final result is comparable to that obtained at 100% H_2O_2 conversion in Exp. 5 (78%). The slightly lower activity of EUROTS-1 in Exp. 7 is probably the result of incomplete calcination. The EUROTS-1 catalysts used in Exps. 1 and 5 were calcined in flowing oxygen and air, respectively. The EUROTS-1 sample used in Exp. 7 was calcined using a same temperature/time profile, but under static conditions in a muffle furnace (Table 1). The static calcination may result in incomplete template removal. It was experienced that as-synthesized EUROTS-1, tested under the reaction conditions of Exp. 1 is totally inactive (no phenol conversion observed after 60 min).

The distribution of the hydroxylated products is also in agreement with the existence of decreased diffusivity in the pores of the ETH-calcined EUROTS-1 sample. The products obtained in Exp. 7 contain more catechol than in Exps. 1 and 5. This can not be a conversion effect, since the higher *o/p* ratio in the products persists after 150 min, when all H_2O_2 is consumed (Table 4).

Use of an internal standard

The use of pentafluorobenzoic acid (PFBA) as internal standard was evaluated at ETH (Table 5). PFBA was selected based on its inertness towards oxidation. Furthermore, the PFBA molecule is too bulky to be able to penetrate into the micropores of TS-1. However, it can be adsorbed on the outer surface of the TS-1 crystals, where it can (1) block non-selective oxidation sites, and (2) obstruct micropore entrances. A comparison of the results obtained in the presence and absence of PFBA (Exps. 6 and 7) suggests that both mechanisms

TABLE 5

Use of PFBA as internal standard with ETH-calcined EUROTS-1 (experimental conditions of Table 2)

Exp.	with PFBA ^a		without PFBA	
	6	150	7	150
Reaction time (min)	60	150	60	150
$X_{\text{H}_2\text{O}_2}$ (%)	100	100	80	100
$S_{\text{hydroxylation, H}_2\text{O}_2}$ (%)	40	30	87	75
$Y_{\text{hydroxylation, phenol}}$ (%)	8	7	16	20
$Y_{\text{hydroxylation, H}_2\text{O}_2}$ (%)	40	30	70	75
<i>Product distribution (mol.-%)</i>				
Catechol	38	40	56	53
Hydroquinone	27	52	40	45
1,4-Benzoquinone	35	8	4	1
<i>o/p</i> ratio	0.6	0.7	1.3	1.1

^a1 g PFBA per g of catalyst.

are operative. This presence of PFBA does not decrease the H_2O_2 conversion, but drastically reduces the hydroxylation yield (Table 5). The small H_2O_2 molecule is still able to penetrate into TS-1 crystals covered with PFBA, whereas for phenol, the accessibility of the interior of the crystals is significantly reduced. Consequently, the hydroxylation yield on H_2O_2 basis has decreased. Hydroquinone is overoxidized to 1,4-benzoquinone, pointing to a reduced diffusivity out of the TS-1 crystals as a result of pore blockage. The *o/p* ratio in the products is low (0.6 after 60 min), indicating that catechol formation on the titanium sites at the external crystal surfaces is also largely suppressed in presence of PFBA.

It can be concluded that PFBA is not a good internal standard, as it alters the activity as well as the selectivity of the catalyst. It is questionable whether any compound exists that can safely be used as internal standard in TS-1 catalysis.

Phenol hydroxylation in methanol

In Exps. 2 and 3, phenol hydroxylation was performed in methanol under identical reaction conditions (Table 2). In Exp. 2, the EUROTS-1 catalyst was calcined under static conditions in a muffle furnace; in Exp. 3 it was calcined in flowing oxygen (Table 1). These differences in catalyst calcination conditions are reflected in the distribution of hydroxylated products (Table 6). As expected, the formation of hydroquinone and 1,4-benzoquinone is suppressed when the calcination of EUROTS-1 is performed under static conditions, re-

TABLE 6

Phenol hydroxylation on KUL-calcined EUROTS-1 in methanol (Reaction conditions of Table 2)

Exp.	2	3	4
Reaction time (min)	60	60	65
X_{phenol} (%)	22	22.5	21
$S_{\text{hydroxylation,phenol}}$ (%)	89	95	66
S_{tar} (wt.-%)	11	-	-
$Y_{\text{hydroxylation,phenol}}$ (%)	20	21	14
<i>Product distribution (mol-%)</i>			
Catechol	49	45	28
Hydroquinone	49	51	64
1,4-Benzoquinone	2	4	8
<i>o/p</i> ratio	1.0	0.8	0.4

TABLE 7

Results of the catalytic testing of TUD-calcined EUROTS-1 (calcination at 400°C, Exp. 8 of Table 2)

Reaction time (min)	60	120	180	240	300	360
$X_{\text{H}_2\text{O}_2}$ (%)	1.5	10	26	24	34	40
$S_{\text{hydroxylation,H}_2\text{O}_2}$ (%)	93	24	25	29	29	33
$Y_{\text{hydroxylation,H}_2\text{O}_2}$ (%)	1.4	2.4	4	7	10	13

TABLE 8

Phenol hydroxylation in methanol solvent on TUD-calcined EUROTS-1 (calcination at 500°C, Exp. 9 of Table 2)

Reaction time (min)	60	120	180	240	300	360
$X_{\text{H}_2\text{O}_2}$ (%)	20	37	61	76	91	94
$S_{\text{hydroxylation,H}_2\text{O}_2}$ (%)	95	91	76	66	59	53
$Y_{\text{hydroxylation,H}_2\text{O}_2}$ (%)	19	34	46	50	54	50
<i>o/p</i> ratio in reaction products	0.09	-	-	-	-	-

sulting in incomplete removal of template or its debris. The fully calcined catalyst used in Exp. 3 is slightly more active and exhibits a higher hydroxylation selectivity. For both types of calcination of EUROTS-1 and in the presence of small amounts of solvent, a replacement of acetone by methanol results in a slight decrease of the *o/p* hydroxylation selectivity (Exp. 3 compared to Exps. 1 and 5; Exp. 2 compared to Exp. 7).

In another experiment (Exp. 4), a large amount of methanol solvent (18 g)

was used (Table 2). After 65 min, 21% of the phenol was converted, this time with hydroxylation selectivity of only 66% (Table 6). Although the tar selectivity was not determined, the low hydroxylation selectivity suggests that tar formation is enhanced when a large amount of methanol solvent is used. Oxidation occurs predominantly in the *p*-position (*o/p* ratio=0.4). Enhanced *p*-selectivities in methanol solvent were previously reported [19,20].

Still higher amounts of solvent and a small amount of catalyst were used in the experiments performed at TUD (Exps. 8 and 9, Table 2). PFBA was used as internal standard. Exps. 8 and 9 were performed under identical reaction conditions, the only difference being the calcination temperature of EUROTS-1 catalyst (Table 1). Calcination at 400°C (Exp. 8) leads to a rather inactive EUROTS-1 catalyst (Table 7), confirming that the removal of the template is essential. The activity is significantly increased after calcination at 500°C (Table 8). After 60 min, the H₂O₂ conversion is low. The hydroxylation selectivity of H₂O₂ exceeds 90%, and the catalyst is highly *p*-selective. The hydroxylation selectivity of H₂O₂ decreases considerably at longer reaction times. It was not determined whether in this instance this is due to H₂O₂ decomposition or increased tar formation. Based on the results of Exps. 4 and 9, it can be concluded that the use of large amounts of methanol enhances the *p*-selectivity of EUROTS-1, at the expense of its hydroxylation selectivity.

CONCLUSIONS

The standard EUROTS-1 catalyst is a phase-pure titanium silicalite-1. The IR and UV spectra of EUROTS-1 contain bands at 960 cm⁻¹ and between 50 000 and 35 000 cm⁻¹, respectively, assigned to zeolitic Ti-O species. Occluded and extracrystalline TiO₂ is absent.

The hydroxylation of phenol with aqueous hydrogen peroxide proves to be an acceptable test reaction. The reaction conditions of Exp. 1 are recommended as standard reaction conditions for the evaluation of the catalytic performance of titanium molecular sieve samples. The reproducibility of phenol hydroxylation under the standard conditions was proven in different laboratories.

The calcination of EUROTS-1 is critical. Uncalcined EUROTS-1 is catalytically inactive. An increase of the calcination temperature from 400 to 500°C results in a substantial increase in activity. Calcination under flowing oxygen or air for 3 h at 550°C leads to the highest hydroxylation activity in acetone and methanol. Static calcination for 3 h at 550°C generates less active catalysts, probably due to incomplete removal of template or its residues. The higher *o/p* ratio in the hydroxylated products observed on EUROTS-1 that is calcined under static conditions is an indication that the active sites in the interior of the crystals are partially blocked.

The addition of pentafluorobenzoic acid (PFBA) to the reaction mixture

significantly reduces the hydroxylation activity and increases the *para*-selectivity. PFBA is probably adsorbed on the external surface of the EUROTS-1 crystals, blocking the non-selective oxidation sites on the external surface, and reducing the accessibility of the micropores for phenol but not for hydrogen peroxide. The use of PFBA or of any other internal standard is accordingly not advisable.

In the presence of small amounts of solvent, a replacement of acetone by methanol results in an increase of the *p*-selectivity of EUROTS-1. This effect is observed for fully as well as incompletely calcined EUROTS-1. The use of large amounts of methanol as solvent enhances significantly the *p*-selectivity of EUROTS-1, at the expense of its hydroxylation selectivity. This effect is not understood at the moment.

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