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The control of selectivity in benzene hydroxylation catalyzed by TS-1: The solvent effect and the role of crystallite size

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ABSTRACT

This paper deals with a study on benzene hydroxylation with hydrogen peroxide, catalyzed by TS-1. The reaction scheme consists of two kinetically parallel primary reactions, leading either to phenol or to benzoquinone. The two diphenol isomers, hydroquinone and catechol, were secondary products, formed on the external sites of TS-1 crystallites (intercrystalline reactivity), and in part in the bulk liquid phase also, because of thermally activated radical reactions. The role of the solvent was examined; because of the presence of methanol/water co-solvents mixture, in three-phase conditions (with two liquid phases) the formation of tar and by-products predominated over the formation of phenol. On the other hand, in two-phase conditions (with a single liquid phase), the selectivity to phenol was higher than 90% at low benzene conversion, but rapidly declined in conditions leading to benzene conversion higher than 3–4%. The kinetically parallel – although chemically consecutive – formation of benzoquinone was minimized by controlling the TS-1 crystallite size; in fact, small-sized TS-1 crystallites produced the highest primary selectivity to phenol. The possible influence of both different titanium environments and defective hydroxyls population was evaluated by means of diffuse reflectance UV–Vis and IR spectroscopy, respectively.

1. Introduction

One reaction of great interest for the chemical industry is the direct hydroxylation of benzene to phenol with hydrogen peroxide (HP) [1–4]. This process, if carried out with good yield and selectivity, could become competitive with the current production of phenol, the main drawback of which is the co-formation of acetone.

A problem with the direct benzene oxidation is the cost of HP; however, this drawback might be overcome by integrating the HP production with the downstream use in benzene oxidation, in the same way as is now done industrially in propene epoxidation. An alternative approach would be the *in situ* generation of HP (directly in the reaction environment where the benzene hydroxylation also takes place), by reaction between hydrogen and oxygen, catalyzed by noble metals, but the selectivity to HP achieved in this reaction is still too low [1,3,5].

Another problem in benzene hydroxylation with HP is the low selectivity to phenol, mainly due to the fact that phenol is more reactive toward oxidation than benzene [1]. This means that overoxidized products – i.e. hydroquinone, catechol and *p*-benzoquinone – are formed too, and therefore a strict control over both reaction conditions and benzene conversion is necessary to achieve an acceptable selectivity to phenol.

Several catalysts have been reported for this reaction [6–19], but one of the best-performing systems is TS-1 [20–29]. However, looking at the literature published on benzene hydroxylation with TS-1, several discrepancies are found, especially with regard to the reaction network, the effect of solvents, and the effect of having either bi-phase or tri-phase reaction systems. Therefore, we decided to carry out a study on the reactivity of TS-1, with the aim of providing a contribution to the understanding of these aspects, the comprehension of which is crucial for developing a more selective and sustainable direct benzene hydroxylation process.

2. Experimental

Various TS-1 samples were prepared (Table 1). Sample TS-1A was prepared following the procedure described in the ENI patent [30]; the crystallite size of this sample was very low (less than 0.2 micron). The slurry containing TS-1 crystallites was spray-dried, after the addition of silica Ludox (10 wt.% with respect to

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Table 1
Catalysts prepared and main characteristics.

Sample	Ti/Si (wt ratio %)	TPAOH/Si (molar ratio)	Preparation procedure	Crystallite size (μm)	Surface area (m^2/g)	UV–Vis bands (nm)
TS-1A	2.0	0.25	Conventional	<0.2[c]	500	210[a]
TS-1B	2.4	1.63	Modified	0.45	615	210[a]
TS-1C	3.2	2.50	Modified	0.40	510	210[a]
TS-1D	3.8	3.00	Modified	0.31	510	210[a], 270[b] (weak)
TS-1E	4.4	1.63	Modified	0.45	534	210[a], 270[b] (strong), 300 (sh)

[a] Assigned to Ti^{IV} in tetrahedral coordination.
[b] Assigned to Ti^{IV} in coordination higher-than-four [22,23].
[c] This sample was used in the form of aggregated particles, with an average particle size of 25 micron.

TiO_2), by using a lab-scale spray-drier LabPlant SD-05 (T of nebulization chamber 200 °C, nozzle diameter 2 mm). The final average size of agglomerated particles was ≈25 μm. The agglomerated samples were then calcined in air at 550 °C.

Conversely, samples TS-1B, C, D and E were prepared using a modified procedure, aimed at obtaining materials characterized by crystallite size in the range of 0.3–0.6 micron. The main parameter changed, when compared to the standard preparation of TS-1, was the TPAOH-to-TEOS ratio in the synthesis sol. In a typical procedure, tetraethylorthotitanate (TEOTi) was dissolved in tetraethylorthosilicate (TEOS); the clear yellow solution obtained was stirred for 15–20 min, then TPAOH (20% aqueous solution) was added. After further stirring, the resulting synthesis gel had the following composition: $1SiO_2{-}aTiO_2{-}b\text{TPAOH}{-}23H_2O$ ($a = 0.0149$, or 0.026 or 0.046; $b = 1.63$, or 2.5 or 3.0). The batch was kept in a water bath at 80 °C for 4 h (for TEOS hydrolysis), then the mixture was topped up to its original volume with deionized water, transferred into a Teflon-lined, stainless-steel autoclave, and heated at 180 °C for 24 h under autogeneous pressure. The autoclave was then cooled and the white gelatinous solution formed was centrifuged at 10,000 rpm for 10 min. The supernatant liquid was discarded, deionized water was added, and the process was repeated 4–5 times until the pH of the supernatant solution was close to neutral. Samples were activated by thermal treatment at 550 °C in air.

The final crystal morphology and dimensions of the TS-1 samples were studied by scanning electron microscopy (SEM) JEOL JSM-T330-A. The silicalite structure was checked by means of powder X-ray diffraction (XRD); diffractograms were recorded using a Phillips PW 1710 diffractometer with Cu Kα radiation.

Fourier transform infrared (FT-IR) spectra were collected at 2 cm^{-1} resolution on a Bruker FT-IR Equinox 55 spectrophotometer equipped with an MCT detector. Samples were studied as either dispersed in KBr pellets or self-supporting wafers. To prepare the latter, powders were pressed into thin pellets (density of about 5 mg cm^{-2}) and pretreated under high vacuum (residual pressure <10^{-3} mbar) using a standard vacuum frame, in an IR cell equipped with KBr windows. To remove moisture and other atmospheric contaminants and to study the hydroxylation degree of the surface, wafers were outgassed for 1 h at 150 °C and 450 °C. To study both Lewis and Brønsted acidic sites, ammonia was used as a probe molecule: in a typical experiment, increasing doses of ammonia (in the 0.01–15 mbar equilibrium pressure range) were introduced into contact with the sample, and then the reversibility of adsorption was checked by 30′ evacuation at room temperature (r.t.).

Diffuse reflectance (DR) UV–Vis spectra were recorded using a Cary 500 Scan UV–Vis NIR spectrophotometer (VARIAN), equipped with an integrating sphere: about 400 mg powder samples were outgassed under high vacuum (residual pressure <10^{-3} mbar) for 1 h at 150 °C and dosed with ammonia at room temperature (1.0–15 mbar equilibrium pressure range). Afterward, reversibility of adsorption was checked by 30′ evacuation at room temperature (r.t.).

Catalytic tests were performed using the following procedure: first, the reactor was loaded with benzene, solvent, and TS-1 catalyst. Then the mixture was heated up to the desired reaction temperature; at this point, the HP aqueous solution was fed to the reactor under stirring, for 30 min, by means of a peristaltic pump; after that, the reaction was left to proceed for 1.5 h more, for an overall reaction time that in standard conditions was 2 h. During this time, HP was also almost completely consumed, as confirmed by iodometric titration; this is also important in order to avoid reactions due to residual unconverted HP when injecting the solution containing the reaction products for GC analysis [31,32], causing misleading determination of the products selectivity. As long as there is no residual HP in the sample, the GC analysis gives highly accurate results as by means of HPLC [28]. On the other hand, we found, by means of preliminary calibration tests, that problems occurring during injection in the GC due to the presence of unconverted HP are avoided when less than 800 ppm HP is present in the injected sample. Therefore, our analytical procedure involved the dilution of the final solution with methanol; this way, even if some residual HP was left after reaction (as inferred by iodometric titration), its concentration was decreased by dilution down to less than 800 ppm. An alternative approach uses MnO_2 for the catalytic decomposition of residual HP into oxygen and water [28]; this method, however, must be used carefully, since the oxidation of some phenolic compound may also occur.

The following amounts of reactants, solvent and catalysts were used, unless otherwise specified: solvent volume (either methanol, or methanol + water, or sulfolane + methanol) 52 mL; HP aqueous solution (35 wt.%) 8.7 mL; benzene 0.1 mol; catalyst 1.17 g. The liquid phase reaction was conducted in a 150-mL batch autoclave made of glass, equipped with a stirrer; heating was provided by means of electric heating elements. The reactor operated at autogenous pressure (4–5 bar for the reaction carried out at 80 °C). We decided to use a sealed reactor (after preliminary tests carried out in an open system, equipped with a refrigerated condenser), because we soon realized that it was not possible to avoid benzene evaporation during reaction. This caused errors in the determination of benzene conversion and therefore made the determination of C balances impossible. With the sealed reactor, C balances were found to always fall between 95% and 105%. In the case of tests carried out in three-phase conditions – which also led to a non-negligible formation of tar – we evaluated the amount of tar produced using a thin film evaporator, which allowed both the removal of monoaromatic compounds and the calculation of the wt yield of tar formed. This method was also systematically applied for the determination of tar in phenol hydroxylation to diphenols. When the reaction mixture was triphasic, we added methanol to the cold slurry containing the reaction components before analysis, and in order to obtain a single liquid phase, the catalyst was separated by means of centrifugation.

For phenol reactivity tests, the following conditions were used: phenol 4.3 mmol; solvent volume (methanol) 50 mL; HP aqueous solution (35 wt.%) 5.6 mL; catalyst 0.45 g. The reactivity test was then conducted with the same procedure used for benzene hydroxylation.

Before injection into the GC instrument, samples were diluted with methanol (typically, 0.5 g of sample was diluted with 25 mL of methanol), in order to decrease the concentration of unconverted HP – the latter having been determined by means of iodometric titration) down to less than 800 ppm. The reaction products were analyzed by means of GC, using a Thermo instrument equipped with FID and a capillary column HP5; oven temperature was programmed from 50° to 250 °C (internal standard: undecane). The error made during catalytic experiments was evaluated after repeating an experiment three times, at the following given conditions: HP (35 wt.%) 8.7 mL; benzene 0.1 mol (8.9 mL, 7.8 g); solvent [water/(methanol + water) = 0.1, vol. fraction] 52 mL; catalyst 1.17 g (TS-1A); temperature 80 °C; reaction time 2 h; benzene/HP 1/1 (molar ratio). Results achieved were: benzene conversion 6.4 ± 0.8 and phenol selectivity 71.3 ± 2.5.

Competitive adsorption experiments were carried out by equilibrating a solution of benzene–phenol (15–1 wt.%) in different solvents (methanol only, methanol/water 5.5/1 wt ratio, methanol/sulfolane 3.8/1 wt ratio) in the presence of TS-1A (6 wt.%), but without HP, for 2 h at 80 °C. Then, the analysis of the liquid phase as determined by GC (internal standard: undecane) was compared with that of the original liquid phase.

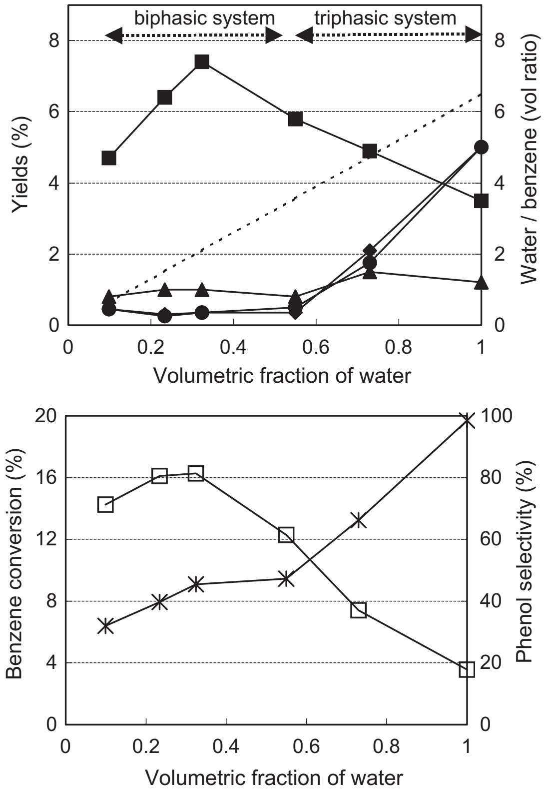

Fig. 1. Effect of the volumetric fraction of water in water + methanol solvent mixture on catalytic performance in benzene hydroxylation. Symbols: yield to phenol (■), CT (♦), HQ (●) BQ (▲), benzene conversion (∗), and selectivity to phenol (□). Dotted line (right-hand scale in top figurer): volumetric water/benzene ratio (included water from HP solution). Reaction conditions: HP (35 wt.%) 8.7 mL; benzene 0.1 mol (8.9 mL, 7.8 g); solvent (water + methanol) 52 mL; catalyst 1.17 g (TS-1A). Temperature 80 °C; reaction time 2 h; benzene/HP 1/1 (molar ratio).

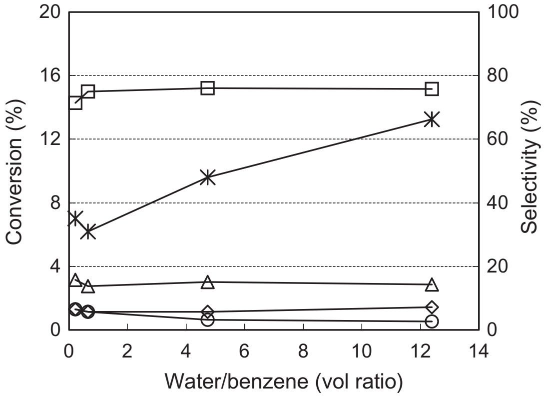

Fig. 2. Effect of the water/benzene volumetric ratio on catalytic performance in benzene hydroxylation. Symbols: benzene conversion (∗), selectivity to phenol (□), CT (◇), HQ (○) and BQ (△). Reaction conditions: HP (35 wt.%) 8.7 mL; benzene 0.1 mol; methanol 52 mL; catalyst 1.17 g (TS-1A); the amount of water was increased (therefore, the total volume changed). Temperature 80 °C; reaction time 2 h; benzene/HP 1/1 (molar ratio); biphasic system.

3. Results

3.1. The role of solvent: biphasic or triphasic?

One controversial point of TS-1 reactivity during benzene oxidation concerns how the presence of either a triphasic or a biphasic system affects the performance. In order to elucidate this aspect, we planned specifically designed experiments. Fig. 1 shows the results of tests carried out keeping the benzene-to-HP molar ratio fixed, and the overall solvent volume also, while varying the relative amount of methanol and water in the solvent mixture (all tests shown in Figs. 1–7 were carried out using the TS-1A sample). The system was biphasic in the left-hand part of the figure (where methanol was the predominant solvent), but was triphasic in the right-hand part (with water as the predominant solvent). Reaction products were phenol, hydroquinone (HQ), catechol (CT) and *p*-benzoquinone (BQ), as is well known from the literature [1–3]; worth of note, there was no formation of *o*-benzoquinone, or of any other oxygenated by-product, that also agrees with literature. In triphasic conditions, tar also formed.

An increasing amount of water led first to an increase in phenol yield, whereas the overall yield to by-products remained substantially constant (this clearly implies an increase in both benzene conversion and phenol selectivity from the initial value of 71% up to 82%, Fig. 1 [bottom]); the maximum yield to phenol achieved was 7.2%. After that, i.e. when the system became triphasic, there was a dramatic increase in the yield of by-products, especially to HQ and CT, and a fall in the yield (and selectivity as well) of phenol; the reaction was also accompanied by the significant formation of tar. BQ formed in amounts greater than diphenols in biphasic medium, but the opposite was true when the reaction was carried out in triphasic conditions. As for the reaction in the biphasic zone, there was an optimum relative amount of methanol and water; with low water content, the yield of phenol was low, and it increased when the molar fraction of methanol was decreased.

In Fig. 2, we report the results of experiments aimed at examining again the effect of an increased water-to-benzene ratio on catalytic behavior; however, tests were carried out by keeping the volume of methanol solvent constant (unlike what we had done in the case of the tests shown in Fig. 1), that is the methanol-to-catalyst ratio, and the benzene-to-HP molar ratio as well, while the amount of water added (and the overall volume solvent) was increased. With these experiments, it was possible to highlight the role of water, while maintaining a biphasic system (because of the presence of an amount of methanol sufficient to dissolve all components); indeed, in the experiments of Fig. 1, the formation

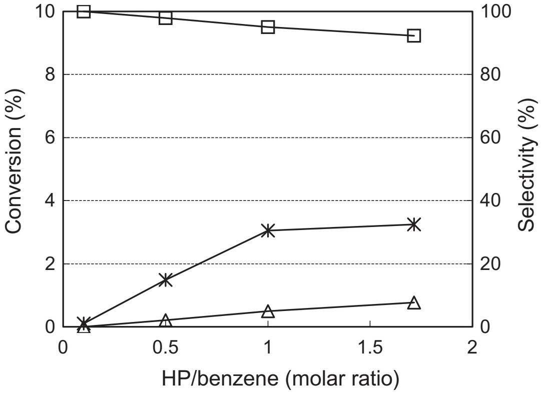

Fig. 3. Effect of the HP/benzene molar ratio on catalytic performance in benzene hydroxylation. Symbols: benzene conversion (∗), selectivity to phenol (□) and BQ (△). Reaction conditions: HP 8.75 mL (at varying concentrations); benzene 0.1 mol; methanol 52 mL; catalyst 1.17 g (TS-1A). Temperature 60 °C; reaction time 2 h. Note that due to the large excess of methanol, the system is always biphasic (single liquid phase).

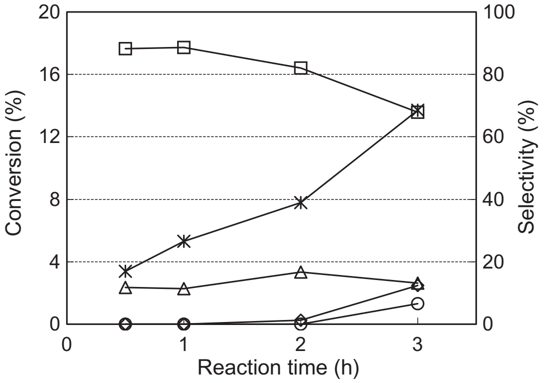

Fig. 4. Effect of reaction time on catalytic performance in benzene hydroxylation with diluted HP solution (3 wt.%). Symbols: benzene conversion (∗), selectivity to phenol (□), CT (◇), HQ (○) and BQ (△). Reaction conditions: HP (3 wt.%) 50 mL; benzene 0.1 mol; methanol 52 mL; catalyst 1.17 g (TS-1A). Temperature 80 °C; benzene/HP 1/1 (molar ratio).

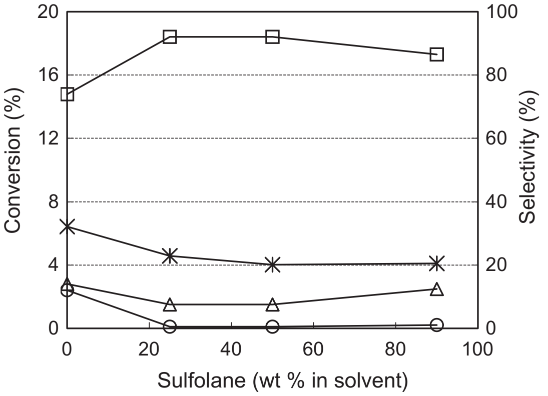

Fig. 5. Effect of the sulfolane content in sulfolane/methanol solvent mixture on catalytic performance in benzene hydroxylation. Symbols: benzene conversion (∗), selectivity to phenol (□), CT + HQ (○), and BQ (△). Reaction conditions: benzene 0.1 mol; solvent (methanol + sulfolane) 52 mL; catalyst 1.17 g (TS-1A). Temperature 80 °C; reaction time: 2 h; benzene/HP 1/1 (molar ratio).

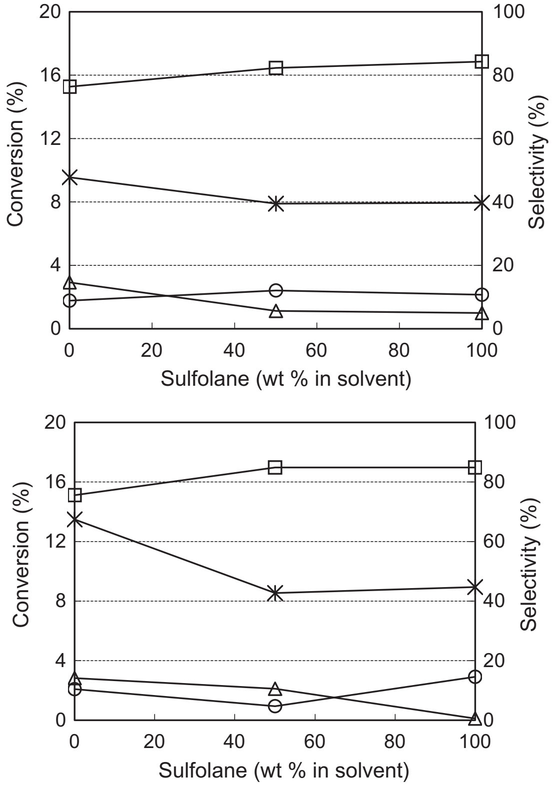

Fig. 6. Effect of the sulfolane content in sulfolane/methanol solvent mixture on catalytic performance in benzene hydroxylation with 7.5% HP (top figure) and with 3% HP (bottom figure). Symbols: benzene conversion (∗), selectivity to phenol (□), CT + HQ (○), and BQ (△). Reaction conditions: benzene 0.1 mol; solvent (methanol + sulfolane) 52 mL; catalyst 1.17 g (TS-1A). Temperature 80 °C; reaction time: 2 h; benzene/HP 1/1 (molar ratio).

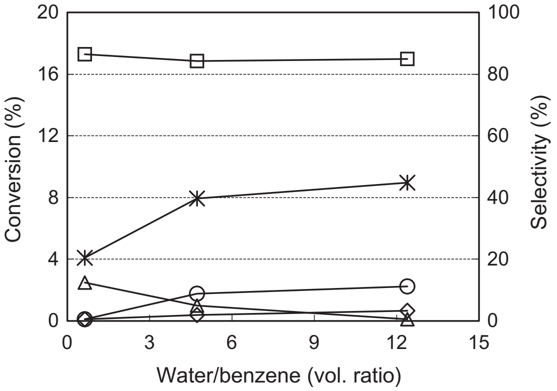

Fig. 7. Effect of the water/benzene volumetric ratio on catalytic performance in benzene hydroxylation. Symbols: benzene conversion (∗), selectivity to phenol (□), CT (◇), HQ (○) and BQ (△). Reaction conditions: benzene 0.1 mol; sulfolane 32 mL; catalyst 1.17 g (TS-1A); the amount of water was increased (therefore, the total volume changed). Temperature 80 °C. Benzene/HP 1/1 (molar ratio).

of the triphasic system, for intermediate values of water molar fraction, may interfere with the effect of solvent variation. Once again, as for tests shown in Fig. 1, benzene conversion increased when the water-to-benzene ratio was increased. The effect on selectivity was less pronounced than in the tests of Fig. 1.

3.2. Analysis of the reaction network

Since the formation of BQ should normally occur by means of a two-step phenol oxidation (first to HQ and then to BQ), it is reasonable to expect that the concentration of HP may affect the distribution of the products. Therefore, tests were carried out using various concentrations of HP; the molar ratio between benzene and HP was changed, but the overall volume of the aqueous solution of HP was kept constant. Reaction time and temperature (2 h and 60 °C) were chosen so as to obtain low benzene conversion and to best highlight the effect of HP concentration on the selectivity to the products of primary oxidation. Moreover, the overall amount of water was kept low, in order to develop biphasic systems throughout all the experiments.

Fig. 3 reports the results of these experiments. In these conditions, there was no formation of CT and HQ, but only of phenol and BQ; the selectivity to this latter compound increased when the molar ratio between benzene and HP was decreased, and correspondingly the selectivity to phenol declined. The increase in HP concentration also accelerated benzene transformation.

These experiments suggest that the phenol formed inside the pores is oxidized to HQ – the formation of CT being unfavored for steric reasons – and HQ is then very quickly transformed into BQ, before it can counterdiffuse toward the bulk phase. In order to confirm this hypothesis, we carried out tests at increasing reaction times by using an HP concentration that permitted only the formation of phenol (the first experimental point in Fig. 3), in order to distinguish between truly primary and secondary products. Fig. 4 shows the results of this experiment, that is, the effect of the reaction time on the selectivity to products. These data confirm the hypothesis stated: CT and HQ both showed the classical behavior of a kinetically secondary product, obtained by the consecutive oxidation of phenol; conversely, BQ was clearly a primary product of oxidation, as it was phenol.

These data suggest that the formation of HQ and CT indeed might occur either at the intercrystalline (external) Ti sites or even in the bulk liquid phase by means of radical reactions between phenol and $^{\cdot}OH$ radicals, because phenol is much more reactive than benzene. Blank experiments made by reacting phenol with hydrogen peroxide, in the same experimental conditions as used for benzene hydroxylation, but without catalyst, led to the following result: phenol conversion 0.8%, with comparable selectivity to CT and HQ. This confirms that a small contribution to phenol consecutive hydroxylation to diphenols may also derive from thermally activated homogeneous reactions.

3.3. The use of sulfolane co-solvent

Fig. 5 compiles the results aimed at understanding the role of sulfolane as the co-solvent; tests were carried out by changing the sulfolane content in the sulfolane/methanol solvent mixture and using 35% HP solution. It is shown that the effect of added sulfolane on BQ selectivity was minimal, whereas the selectivity to diphenols went down to almost zero. The selectivity to phenol was the higher with 25–50 wt.% sulfolane in the solvent mixture. There was also an effect on conversion, which decreased; however, this change was not great enough to be the only one responsible for the drastic fall in selectivity to diphenols.

Results of experiments carried out with diluted HP solutions are illustrated in Fig. 6a (HP solution 7.5%) and 6b (HP solution 3%); in these experiments, the benzene-to-HP ratio was always 1, whereas the water-to-benzene ratio increased, due to the use of the diluted HP solution. The effect of sulfolane with the 7.5% HP solution was the opposite of that obtained with the concentrated HP solution (shown in Fig. 5). There was a remarkable effect on BQ selectivity (which decreased when the 50% sulfolane was used), whereas there was no effect on the selectivity to CT + HQ. Less clear is the effect of sulfolane with extremely diluted HP solutions, that is, in conditions leading to the triphasic system (Fig. 6b). In this case, the presence of 50% sulfolane led to a drastic fall in benzene conversion and to an increase in the selectivity to phenol, with a corresponding decrease in selectivity to both BQ and CT + HQ; with only sulfolane solvent, however, the selectivity to BQ became nil, whereas that to diphenols increased remarkably.

Finally, Fig. 7 sums up the results achieved with 90–100% sulfolane solvent (that is, with nil or a very small amount of methanol), while increasing the HP concentration (that is, decreasing the water/benzene ratio, while keeping the HP/benzene molar ratio constant). It is interesting to compare this figure with the results plotted in Fig. 2, where the effect of the same parameter, water/benzene ratio, on the reactivity behavior is reported, for tests carried out in methanol solvent. It is shown that in both cases an increase in the water/benzene ratio led to an increase in benzene conversion.

3.4. Competitive adsorption of benzene and phenol

Competitive adsorption tests were carried out by equilibrating liquid mixtures of different compositions in the presence of TS-1A, without HP. Mixtures were mixed for 2 h at 80 °C, in a closed vessel; then the final bulk liquid phase was analyzed and its composition was compared with that of the starting mixture. The aim was to find out how the nature of solvents used affected the distribution of selected compounds between the liquid phase and TS-1. Results of these experiments are compared in Table 2, which shows the relative variation in concentration of the aromatic components in the bulk liquid phase after equilibration. The behavior of the mixtures containing either sulfolane or water as co-solvents for methanol appears to be very similar, whereas the use of methanol, the less polar solvent, alone led to the preferred adsorption of phenol, which showed the greatest relative change of concentration in the liquid phase. This indicates that the competitive adsorption in hydrophobic TS-1 was controlled by the solvent characteristics.

3.5. The role of crystallite size

The preparation of Ti–silicalite by the conventional synthesis method (sample TS-1A) leads to crystallites of an extremely low size, which must be agglomerated into bigger particles in order to allow the filtration of the used catalyst from the reaction batch. In order to study the effect of the crystallite size on the primary selectivity in benzene oxidation, we set up a modified synthetic protocol for TS-1. This protocol allowed the formation of larger crystallites than those obtained with the conventional procedure and, lastly, permitted the use of TS-1 for reactivity experiments, without the need for agglomeration into larger particles. Furthermore, we found that by using a TPAOH-to-TEOS ratio higher than 1, it was possible to control the crystallite size of TS-1. This is shown in Table 1, which summarizes the main features of the samples synthesized with the modified procedure; XRD, FT-IR and Raman spectroscopy all confirmed the formation of original, well-crystallized TS-1 samples, with no formation of segregated anatase (with the exception of sample TS-1E).

Table 2
Results of competitive adsorption experiments with TS-1A.

Experiment number	Composition of the initial mixture	Change of aromatics concentration in the bulk liquid phase after equilibration
1	Methanol, benzene, phenol, TS-1	Benzene – 1% Phenol – 21%
2	Methanol, water, benzene, phenol, TS-1	Benzene – 12% Phenol – 14%
3	Methanol, sulfolane, benzene, phenol, TS-1	Benzene – 14% Phenol – 13%

The values reported in Table 1 show that

1. The crystal size was affected exclusively by the TPAOH/TEOS molar ratio (that is, the TPAOH/Si ratio), regardless of the Ti/Si ratio used (compare samples TS-1B and TS-1E). An increase in the TPAOH/Si ratio led to a non-negligible, systematic effect on the crystal size; the latter was the smallest in samples prepared using the highest TPAOH/Si ratio. Therefore, it is evident that large amounts of TPAOH facilitate the nucleation process when compared to the crystallite growth process.
2. All samples show the band at 210 nm, which is attributed to tetrahedral Ti^{IV} incorporated within the silicalite framework. However, in samples TS-1D and TS-1E (especially the latter), an additional band at 270 nm was present: in the literature, this event is attributed to the formation of a Ti center with an enlarged coordination sphere, but still isolated in the silicalite matrix [28,33–35].

Catalytic experiments carried out on samples synthesized with the modified procedure are summarized in Fig. 8, plotting the crystallite size, the conversion of benzene, and the selectivity to phenol on the basis of the Ti/Si wt ratio. There was no clear relationship between the overall benzene conversion and sample features, probably because conversion was a complex function of various structural and chemical features, i.e. the Ti/Si ratio (which also affected the hydrophilicity of samples, see characterization of Ti species) and the crystallite size. In fact, TS-1C was more active than TS-1B: this may be attributed to the higher amount of framework Ti (in both samples, the only Ti species was the tetrahedral one), but TS-1D was as active as TS-1B, despite both the higher Ti content and the presence of pentacoordinated Ti species, which are considered to be especially active species [22,23]. One distinguishing feature of TS-1D was the lower crystallite size, which means a shorter mean intracrystalline path for reactants and products and thus a lower effective reaction time constant. In the case of TS-1E, not only the high Ti content and the presence of a fairly intense band at 270 nm, but also a large crystallite size, are all factors that may contribute to obtaining the highest conversion of benzene.

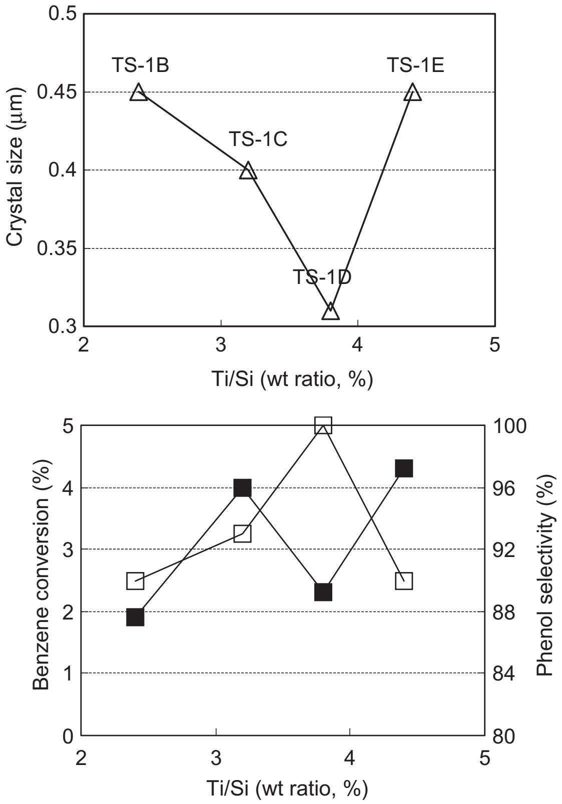

Fig. 8. Plot of crystal size (top figure) and of benzene conversion (■) and phenol selectivity (□) (bottom figure) in function of the Ti/Si ratio used for samples preparation (see Table 1 for main samples characteristics). Reaction conditions: HP (35 wt.%) 8.7 mL; benzene 0.1 mol (8.9 mL, 7.8 g); methanol 52 mL; catalyst 1.17 g (TS-1A). Temperature 80 °C; reaction time 2 h; benzene/HP 1/1 (molar ratio).

However, for our purposes, the conversion achieved itself is not so important; the aim of these experiments, in fact, was that of comparing the selectivity to the products of primary benzene oxidation: Fig. 8 shows that there was a clear inverse relationship between the crystallite size and the selectivity to phenol.

3.6. The reactivity in phenol hydroxylation

We conducted experiments aiming to confirm the role of crystallite size on catalytic behavior in benzene hydroxylation. Specifically, reactivity tests were carried out using phenol as reactant, under the same reaction conditions as used for benzene hydroxylation experiments. It should be noted that these conditions are not the optimal ones typically used for the synthesis of diphenols by phenol hydroxylation with TS-1; in the latter case, in fact, a mixture of acetone and water is the reaction solvent, and a 60% HP solution is used.

Results of experiments are summarized in Table 3. The main differences when compared to the synthesis of diphenols, when carried out at the optimal reaction conditions, concern the formation of BQ [2,36,37]. The latter forms in negligible amounts in the process for diphenol production, but it is the prevailing product in the experiments described in the present work. Also, the considerable formation of tar is attributable to the fact that water and methanol, unlike acetone, are not good solvents for tar [37]. As for differences among the various TS-1 samples, the following is worth mentioning: (a) the yield to BQ was by far the lowest with TS-1D, which also produced no diphenols, but a significant amount of tar; (b) TS-1B, TS-1C and TS-1E showed a similar behavior with regard to the formation of BQ, but the yield to diphenols and tar shown by these samples was very different.

3.7. UV–Vis and IR spectroscopic characterization of Ti species

Fig. 9a shows the DR UV–Vis spectra of TS-1B, TS-1D and TS-1E powders both (i) outgassed at 150 °C and (ii) under approximately 15 mbar ammonia equilibrium pressure (bold curves).

The spectra of samples outgassed at 150 °C show a main absorption band at 205–210 nm, assigned in the literature to $Ti^{4+}O^{2-} \rightarrow Ti^{3+}O^{-}$ charge-transfer of highly dispersed tetrahedral TiO_4 species, incorporated within the framework [38,39]; as expected, the overall intensity of absorption increases with the titanium content (Table 1). The two samples with the highest titanium content, i.e. TS-1D and TS-1E, show an additional band at 270 nm that, according to the literature, are assigned to very reactive titanium species in a coordination higher-than-four formed in the TS-1 obtained by the modified synthetic procedure [22,23]; other possible assignments for the 270 nm band are either

Table 3
Reactivity of TS-1 catalysts in phenol hydroxylation.

Sample	BQ yield (%)	CT + HQ yield (%)	Tar yield (%)
TS-1B	16	2	41
TS-1C	24	6	10
TS-1D	4	0	26
TS-1E	16	0	17

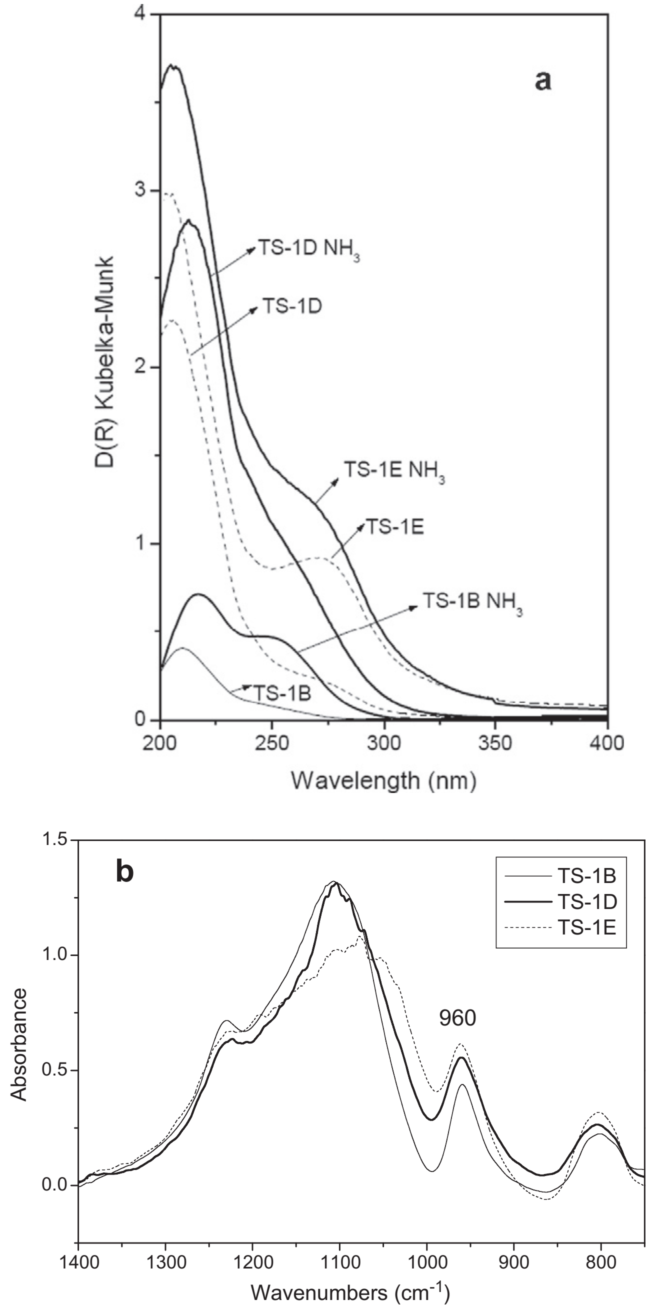

Fig. 9. (a) DR UV–Vis spectra of TS-1B, TS-1D and TS-1E powders outgassed at 150 °C and under approximately 15 mbar NH_3 equilibrium pressure (curves labeled as TS-1B NH_3, TS-1D NH_3 and TS-1E NH_3). (b) FT-IR spectra, in the 1400–750 cm^{-1} range of TS-1B (continuous line), TS-1D (bold line) and TS-1E (dotted line) powders dispersed in KBr pellets.

partly aggregated hexacoordinated Ti–O–Ti species or isolated single-bonded TiO_x species attached to the zeolite lattice [40]. With TS-1E, a further absorption is observed above 300 nm, indicating that the formation of Ti–O–Ti groups (e.g. extra-framework TiO_2) [41] occurs at the highest titanium loading.

Dosage of ammonia brings about an overall absorption intensification and a red-shift of the 210 nm band, with the formation of a shoulder at about 245 nm, due to an increase in titanium coordination that can lead to the formation of octahedral Ti complexes in which two ammonia molecules are coordinated by each Ti^{IV} site [38]. Ammonia adsorption was not reversible by outgassing at room temperature (spectra not reported for the sake of clarity), indicating that this moiety interacts strongly with tetrahedral Ti species, increasing their coordination state. The 270 nm band seems to be not too affected by the presence of ammonia, thus confirming that the corresponding titanium species are in a higher-than-four coordination state and therefore less prone to interact with another ligand.

The presence of framework tetrahedral titanium species is confirmed in Fig. 9b by the IR spectra of the samples dispersed in KBr pellets: in addition to the bands of asymmetric and symmetric stretch vibrations of Si–O–Si groups in the silica matrix [42], the spectra reported in Fig. 9b show a band at 960 cm^{-1}, readily assigned to the asymmetric stretch mode of Si–O–Ti bridges. According to the literature, the latter band may be considered a fingerprint of the presence of tetrahedral Ti species in the framework [42]. On the other hand, the shift of the asymmetric Si–O–Si stretch band toward lower wavenumbers with increasing titanium loading suggests the formation of extra-framework TiO_x species.

Fig. 10a reports IR spectra in the OH stretch range (3800–3000 cm^{-1}) of self-supporting wafers outgassed at 150 °C and 450 °C: all spectra were normalized to unit weight to allow comparison and were stacked for the sake of clarity. The spectra of samples outgassed at 150 °C (upper curves) show components at 3740, 3727, 3700 cm^{-1} and a broad absorption extending below 3600 cm^{-1}. These features are assigned respectively to the presence of (i) free isolated silanols on the outer surface of crystals (3740 cm^{-1}); (ii) free isolated silanols inside Ti–silicalite cavities (3727 cm^{-1}); (iii) terminal H-bonded silanols of hydroxyl nests located inside micro-channels (3700 cm^{-1}); and (iv) H-bonded silanols inside hydroxyl nests [43]. Outgassing at 450 °C (lower curves) brings about an overall decrease in band intensity due to dehydration, in particular as far as OH species belonging to hydroxyl nests are concerned, in keeping with their high reactivity.

The comparison among samples shows that, as a whole, TS-1E has a higher amount of defective hydroxyls, as indicated by the much higher intensity of the broad absorption extending below 3600 cm^{-1}.

The acidity of both Lewis and Brønsted surface species was studied by means of ammonia adsorption at room temperature: Fig. 10b shows IR difference spectra recorded after dosing NH_3 (equilibrium pressures in the 0.1–15 mbar range) on the TS-1E sample outgassed at 150 °C. Difference spectra were obtained by subtracting the spectrum of the bare sample reported in Fig. 10a; therefore, the negative bands in Fig. 10b correspond to species disappearing upon interaction with NH_3 molecules and positive bands are the corresponding features of ammonia adducts.

Dosage of NH_3 brings about the formation of two main bands at 1457 cm^{-1} (with a component forming at higher pressure at approx. 1490 cm^{-1}) and at 1607 cm^{-1}. The former is due to ammonium species formed by the interaction of ammonia with Brønsted acidic sites, as confirmed by the corresponding negative bands observed in the OH stretch region. It may be inferred that at least two kinds of Brønsted hydroxyls with different acidic strengths occur on the surface of the TS-1E sample: this is shown by both the presence of two components (at 1457 and 1490 cm^{-1}) and the fact that after 30′ evacuation at room temperature, the 1457 cm^{-1} band is still present (dotted spectrum). The latter band is therefore assigned to ammonium species, which are formed after reaction with more acidic hydroxyls, most probably TiOH species, and the component at 1490 cm^{-1} to ammonia molecules reacting with less acidic species, i.e. nest hydroxyls [44]. The presence of Lewis acidic sites along with Brønsted hydroxyls is confirmed by the band at 1607 cm^{-1}, assigned to ammonia molecules interacting with Ti^{IV} sites [45].

At higher pressures another component shows up at 1625 cm^{-1}, due to ammonia molecules H-bonded to less acidic isolated silanols

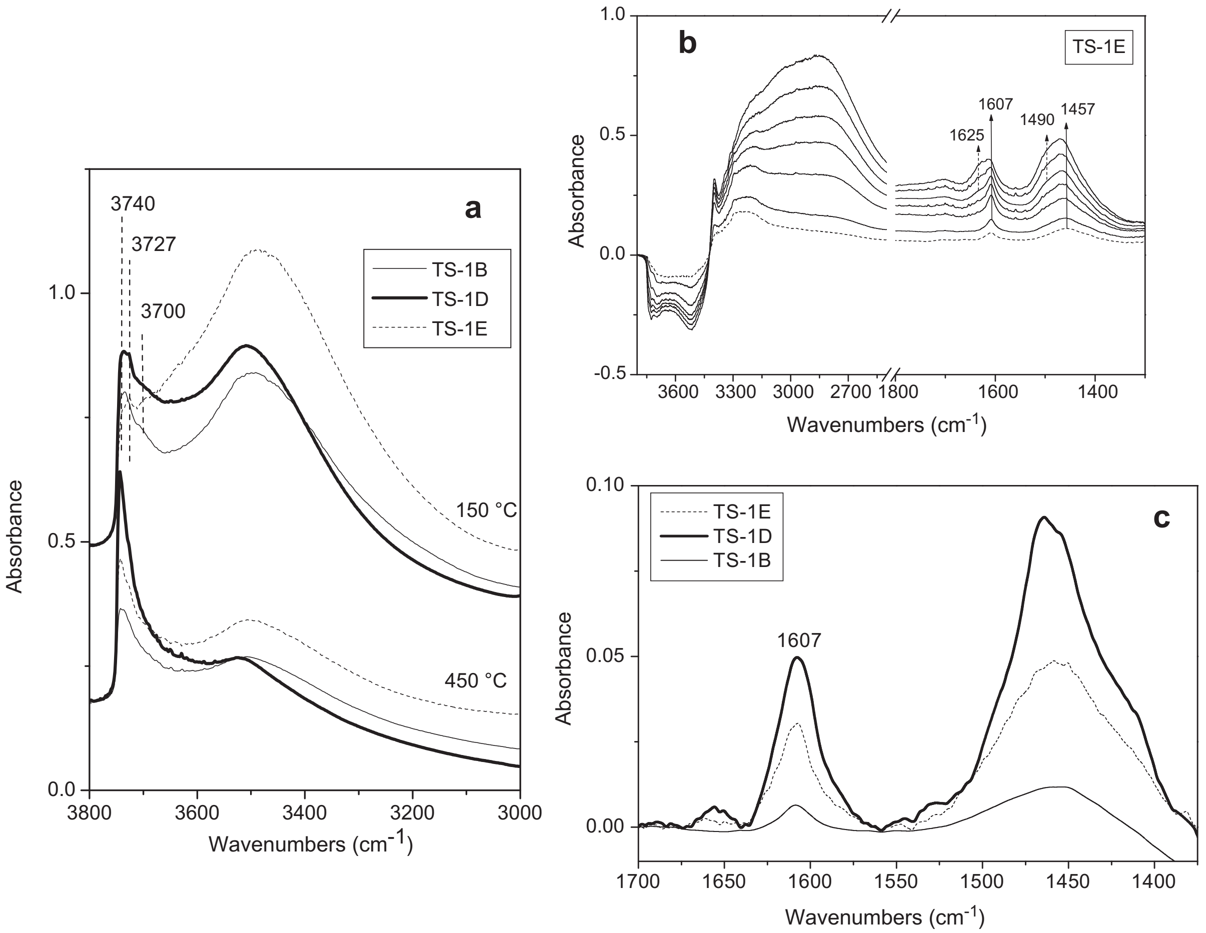

Fig. 10. (a) FT-IR spectra in the 3800–3000 cm^{-1} range of TS-1B (continuous line), TS-1D (bold line) and TS-1E (dotted line) self-supporting wafers outgassed at 150 °C (upper curves) and 450 °C (lower curves). (b) Difference spectra recorded after dosing increasing pressures of ammonia (0.1–15 mbar range) on TS-1E sample outgassed at 450 °C; the dotted line corresponds to the spectrum recorded after outgassing for about 30' at room temperature. (c) Comparison of normalized difference spectra in the NH bending region recorded on samples TS-1B (continuous line), TS-1D (bold line) and TS-1E (dotted line) outgassed for about 30′ at room temperature after dosing approximately 15 mbar ammonia.

originally absorbing at 3740 cm^{-1} (negative band in the figure) [45]. After prolonged evacuation at room temperature (dotted curve), the adsorption of ammonia proved to be not completely reversible, thus indicating the presence of rather strong Brønsted and Lewis sites, due to TiOH and Ti^{IV} species, respectively.

Dosage of ammonia on the TS-1E sample outgassed at 450 °C (spectra not reported for the sake of brevity) shows the presence both of Lewis acidic sites (band at 1607 cm^{-1}) and of a band at 1480 cm^{-1} due to fewer ammonium species: this latter phenomenon is due to surface dehydroxylation, with the removal of most acidic (i.e. reactive) hydroxyls, since the component at 1457 cm^{-1} due to TiOH species is no longer seen and only the features of ammonia reacting with silanols are observed. The latter interaction is indeed reversible by evacuation at room temperature. Similar IR features were observed with both the TS-1B and TS-1D samples: Fig. 10c compares difference spectra in the 1700–1375 cm^{-1} range recorded on samples evacuated at room temperature after ammonia dosage; difference spectra were obtained by subtracting the spectra of the bare samples outgassed at 150 °C which are shown in Fig. 10b. The same features ascribable to the presence of titanium are seen: two main bands are observed at 1607 cm^{-1} and 1457 cm^{-1}, assigned respectively to ammonia molecules interacting with Ti^{IV} Lewis sites and to ammonium species formed upon interaction with TiOH Brønsted hydroxyls. Although sample TS-1E has the highest Ti content, it does not show the most intense bands due to ammonia adsorbed on titanium sites, showing that a fraction of titanium is not accessible to this probe and therefore is less reactive.

4. Discussion

4.1. The reaction scheme in benzene hydroxylation: intraparticle and interparticle products

From the literature, it is not possible to infer a clear picture of the reaction network for benzene hydroxylation [1–3]; in general, it is reported that by-products of the reaction are HQ, CT, BQ and tar, and that the less sterically hindered HQ and BQ may preferentially form inside TS-1 pores, whereas the formation of bulkier CT occurs on external sites. However, no scheme showing kinetic relationships between the various products has been reported.

Experiments reported in Fig. 4 clearly indicate that the only primary products of benzene oxidation are phenol and BQ (at least, when diluted HP solutions are used). Therefore, a fraction of phenol, once formed at intracrystalline Ti sites, is oxidized into HQ (the formation of CT being disadvantaged because of steric reasons) and then quickly to BQ before it can leave the porous TS-1 structure. The fast oxidation of HQ into BQ entails the homolythic scission of the HO–φ–O–H bond to generate HO–φ–O$^{\cdot}$, catalyzed inside TS-1 pores by Ti–O$^{\cdot}$ sites. With regard to the primary formation of phenol, this product may be formed either on external, intercrystalline Ti sites or inside the porous structure of TS-1, thereafter counterdiffusing toward the liquid phase before the occurrence of any further oxidation (e.g. primary oxidation might occur in pore mouths).

With regard to the behavior of HQ and CT, results shown in Figs. 1 and 2 evidence similar behaviors for the two isomers in response to changes in solvent composition, thus suggesting that the formation of both compounds occurs over the same types of sites, either intracrystalline or intercrystalline. After phenol has formed, it may either diffuse into the porous structure and therein react – a phenomenon especially favored in water solvent [37] – or more likely react over the external sites, or even in the bulk liquid phase by thermal activation, finally yielding the two dihydroxylated isomers. In fact, if the consecutive oxidation of phenol to HQ occurred inside pores, the latter should be oxidized quickly up to BQ; as a matter of fact, our results clearly indicate that there is no kinetic relationship between HQ and BQ. It is worth noting that a similar behavior (i.e. primary formation of BQ, secondary formation of both HQ and CT) was recently reported for the same reaction when catalyzed by TS-1 PQ [28], with an initial selectivity to phenol and BQ higher than zero; however, this result was not discussed in that paper.

An important implication for this result is that the only intracrystalline product of the reaction is BQ (and maybe also phenol), whereas CT and HQ are likely to be intercrystalline products. Therefore, it is expected that the crystal size of TS-1 may affect the ratio between phenol and BQ, because smaller crystals will lead to a higher initial selectivity to phenol, and a lower selectivity to BQ. This may be due to the fact that either a smaller intracrystalline residence time would limit any further oxidation of phenol to HQ and then to BQ (in fact, a shorter mean path for the counterdiffusion of phenol toward the bulk liquid phase would make any consecutive phenol oxidation less likely), or the contribution of external Ti sites would be increased with smaller crystallites: an event that might foster the formation of phenol with respect to BQ if the former compound is formed over external Ti sites.

In the case of the TS-1A sample used for these experiments – which is made of particles of ≈25-micron average size and prepared by spray-drying and agglomeration of very small crystallites (of a size smaller than 0.2 micron) – the mean path of products is evidently very long: something that – in principle – should enhance the formation of BQ, with a lower primary selectivity to the desired phenol. These results anticipate that one key event for increasing the selectivity to phenol is shortening the mean path within pores. On the other hand, the formation of the kinetically secondary products, HQ and CT, is expected to depend mainly on both benzene conversion and the characteristics of external surface sites.

4.2. The role of solvent: (a) water vs methanol and (b) sulfolane as methanol co-solvent, in relation to the reaction network

In the case of phenol hydroxylation into diphenols, phenol transformation was found to be governed by intracrystalline diffusion in large crystals of TS-1 [36]; a strong diffusion-limited transformation of phenol supports our hypothesis that with larger crystallite size the consecutive transformation of HQ into BQ has the time to occur, finally yielding BQ as a primary product of benzene oxidation. The same authors excluded a major influence of external surface activity. Tuel et al. [46] concluded that in phenol hydroxylation the product ratio of HQ to CT is mainly controlled by the external surface activity; HQ and CT were thought to be the preferred reaction products in the micropores of TS-1 and on the external surface Ti sites, respectively. Wilkenhöner et al. [37] investigated the effect of solvent and of TS-1 crystallite size on the catalytic behavior in phenol hydroxylation. The presence of diffusional constraints for the conversion of phenol and geometric constraints for the formation of CT were highlighted; on the other hand, with small crystals, the external surface sites were reported to contribute significantly to the total rate of reaction and its selectivity. The inertization or selective poisoning of the external surface of TS-1 led to a decrease in the formation of tar and a slight increase in the selectivity to HQ; however, the role of external sites was dependent on the type of solvent used. While HQ was the predominant product in the pores of TS-1, the main product formed on the external surface was CT in acetone solvent and HQ in protic solvents [37].

In our case, the ratio between the two isomers, formed during benzene hydroxylation, changed a great deal depending on the type of solvents used (see, for instance, Figs. 1, 2 and 7): an observation in line with literature findings. However, the plot in Fig. 4, reporting the effect of reaction time on the selectivity to products with only methanol solvent (apart from the water contained in the diluted HP solution), shows that the selectivity to CT was twice that of HQ over the entire reaction time range examined. This supports the absence of any shape-selectivity effect, as well as the hypothesis that the two diphenol isomers are formed mainly as kinetically secondary products on the external Ti sites.

Our data demonstrate that the solvent affects both conversion and selectivity to products in benzene hydroxylation. Literature is in agreement on the fact that the nature of the solvent is essential and is also the major parameter affecting catalytic performance [1,2]. Solvents capable of homogenizing the hydrophobic substrate and the aqueous HP, such as acetone, acetonitrile or *t*-butanol, make it possible to achieve optimum performances. In general, more polar solvents have little interaction with the hydrophobic surface of TS-1, especially in samples having fewer defects and surface hydroxyl groups. Therefore, with polar solvents the pores are preferentially filled with apolar hydrocarbons (e.g. benzene). The opposite is true with less polar solvents (e.g. *t*-butanol); the partition coefficient is modified, and this clearly has implications on the reaction rate. Another important point is the interaction between the solvent and the active sites. For example, it is well known that methanol itself, although showing little affinity for the TS-1 due to its predominantly polar characteristics, may interact with Ti^{IV} and contribute to the formation of a pentacoordinated site in which the positive charge on the O atom of the hydroperoxo species forms by interaction with the methanol proton [2].

With regard to the effect of having either a biphasic or a triphasic system, Kumar et al. [24–27] reported that the presence of a triphasic system (two liquid phases and the solid catalyst) yields an excellent performance. Other authors, however, did not confirm this result [22,28]. Our results indeed show that in the conditions examined, the presence of a triphasic system has negative effects on the catalytic behavior (Fig. 1). As for the reaction in the biphasic zone, with low water content, the yield of phenol was low; benzene conversion and yield to phenol increased when the molar fraction of methanol was decreased within the biphasic zone. The same effect is observed in the case of experiments reported in Fig. 2, carried out under conditions leading to a biphasic system; benzene conversion increased when the water-to-benzene ratio was increased; however, for a similar interval of variation in this feed ratio (i.e. from 1 to 3), there was only a lower increase in conversion compared to that observed for the tests in Fig. 1.

The increase in benzene conversion, observed in the biphasic zone for increasing amounts of water, was due to the fact that a more polar solution (because of an higher molar fraction of water) may increase the concentration of benzene within pores, an effect attributable to the zeolite property of performing a selection of molecules from the liquid phase by acting as an additional solvent for the reaction [47]. This leads to a higher rate of benzene conversion and phenol formation (provided HP does not become the limiting reactant). This hypothesis is confirmed by the results of competitive adsorption tests reported in Table 2. The concentration of benzene and phenol inside TS-1 is affected by the nature of solvent used; with more polar solvent mixtures (either methanol/water or methanol/sulfolane), benzene and phenol are equally retained inside TS-1 pores, whereas when only methanol is used, the interaction of TS-1 with phenol predominates over that of benzene. In other words, with more polar solvent mixtures, benzene has more affinity for TS-1 than for the liquid bulk phase, whereas with a less polar solvent, benzene does not compete so much with phenol for diffusion inside the TS-1 pores. On the other hand, phenol is soluble both in more polar methanol/water(sulfolane) mixtures and in methanol only.

Sulfolane co-solvent also shows a significant effect on catalytic behavior. In literature, it is reported that the coordination of phenol by sulfolane inside the TS-1 pores limits its consecutive hydroxylation to CT and HQ [1,3,22]. Authors from the ENI research team hypothesize that the increased selectivity may be due to the formation of a sterically hindered species that cannot enter the TS-1 pores, thus allowing phenol to remain relatively protected against further oxidation [22,23]. The hypothesis of a bulky complex with sulfolane would fit perfectly with our results and with the hypothesis of BQ as the only intracrystalline by-product, in the case sulfolane had an effect only on CT and HQ (formed on Ti intercrystalline sites), and not on BQ (formed inside the TS-1 microporosity). In other words, we hypothesize that the coordination effect of sulfolane plays out of TS-1 pores, and not inside them, thus keeping phenol from consecutive oxidation to either CT or HQ. This is not so much due to steric reasons, but rather probably to the fact that sulfolane is a polar molecule (notwithstanding the apolar C_4 part) which is soluble in water, and its access in TS-1 hydrophobic pores is probably not allowed, at least as long as less polar molecules (e.g. methanol) are present in the reaction medium. Less polar molecules have preferential access to the TS-1 pores, and then sulfolane would remain in the bulk liquid. Results shown in Fig. 5 – obtained under conditions inhibiting the access of sulfolane to the TS-1 porous system, because concentrated HP was used, and the amount of methanol solvent was largely predominant over the amount of water - support our hypothesis. The main effect of sulfolane co-solvent in methanol/sulfolane mixtures was that of decreasing the selectivity to diphenols that went down to almost zero, whereas the effect on BQ selectivity was minimal.

On the other hand, when sulfolane was used as co-solvent in diluted HP solutions (Fig. 6), with the amount of water solvent predominating over the amount of methanol, e.g. with diluted HP solutions (while the HP-to-benzene ratio was constant), under conditions more favorable for the access of sulfolane to pores, the effect of sulfolane was quite different from that obtained with negligible amount of water solvent. In fact, there was a remarkable decrease in BQ selectivity, whereas there was no effect on selectivity to diphenols. This provides a clear indication that in reaction conditions which are more conducive to the diffusion of sulfolane into the TS-1 pores, sulfolane yields an enhancement effect on the selectivity to the by-products formed within pores (BQ), but a less marked effect on those formed outside the TS-1 crystallites.

As summarized in Fig. 7, the relative amounts of sulfolane, methanol and water have a profound influence on catalytic behavior; higher water-to-benzene ratio (at low HP concentration) leads to higher values of benzene conversion. The amount of water in the reaction medium influences the amount of both methanol and sulfolane inside TS-1 pores; therefore, depending on the amount of water used, sulfolane plays its protecting role on phenol either in the bulk liquid phase or inside TS-1 pores.

4.3. How prepare a more selective TS-1 catalyst: the role of crystallite size and of nature of Ti sites

Data reported in Fig. 8 show that the crystallite size is an important parameter affecting catalytic behavior. It is worth noting that all these samples showed a lower activity than that of sample TS-1A. In conditions that, with the latter catalyst, led to a benzene conversion of 6.4%, with 75% selectivity to phenol (selectivity to BQ 12%, to CT + HQ 13%) (see Fig. 1 bottom), all samples prepared with the modified procedure resulted in less than 4.5% benzene conversion. However, the low conversion achieved makes it possible to compare samples in conditions that led to the exclusive formation of BQ and phenol, with nil formation of CT + HQ. In fact, in the conversion range of all our samples, the only reactions occurring are the parallel ones leading to phenol and BQ, with nil contribution of consecutive reactions leading to CT and HQ (the selectivity to these latter compounds was nil). In other words, in the conversion range examined, the selectivity to phenol (and to BQ as well) was not a function of benzene conversion, but only of the ratio between the rates of the two kinetically parallel reactions:

1. Benzene → phenol
2. Benzene → (phenol → HQ →) BQ

in which reaction 2 is made up of chemically consecutive steps, but appears as a direct, single-step reaction from a kinetic standpoint. This allows comparing the selectivity to the primary products in function of the crystallite size. The inverse relationship found between the latter and the selectivity to phenol (Fig. 8) is in agreement with our hypothesis, that the counterdiffusion path length of phenol toward the bulk phase greatly affects the probability that phenol may undergo the chemically consecutive transformation into HQ and then BQ; the longer the path, the higher the selectivity to BQ and the lower to phenol.

Tests made by reacting phenol confirm this hypothesis (Table 3). TS-1D, the sample showing the higher initial selectivity to phenol and nil formation of BQ in benzene hydroxylation, produced the smallest amount of BQ when the reaction was carried out starting from phenol. Notably, the same catalyst also produced a negligible amount of diphenols but rather significant amounts of tar. Therefore, because of its lower crystallite size, and despite the relatively high amount of Ti, the rate of phenol transformation to HQ and BQ inside the TS-1D pores is low, because the effective intracrystalline contact time is low if compared to TS-1 samples having greater crystallite size. On the other hand, reactions occurring on external sites lead to tar formation.

In samples with the largest crystallite size, the formation of BQ by the two-step intracrystalline oxidation of phenol is much more significant than with TS-1D. On the other hand, samples TS-1B, TS-1C, and TS-1E show more important differences with regard to the formation of diphenols and tar. This supports the hypothesis that the formation of BQ (not very different in the three samples) occurs on different sites than the formation of the other by-products.

The reactivity of TS-1E appears anomalous. On the one hand, the yield to BQ is the same as that of TS-1B, which is perfectly in line with the similar crystallite size of the two samples (which also show similar selectivity to phenol and BQ in benzene hydroxylation, Fig. 8). On the other hand, the selectivity to CT and HQ is nil (as it is also for TS-1D), and the yield to tar is rather significant.

IR spectroscopy has shown that TS-1E, the sample with the highest titanium content, has also the highest amount of hydroxyls nests: according to the literature [48], the intensity of the silanol nests band in TS-1 should decrease with an increasing amount of framework titanium, since Ti insertion into the TS-1 network is accompanied by the progressive reduction of Si vacancies, i.e. hydroxyl nests, with formation of both [TiO_4] and [$(SiO)_3TiOH$] sites. Previous EXAFS studies also indicated that in TS-1 samples prepared by traditional synthesis the fraction of defective [$(SiO)_3TiOH$] sites progressively decreases upon increasing Ti content [48]. In the present case, however, the modified synthesis procedure adopted could lead to slightly different titanium environments along with different hydroxyl populations, as well. In fact, although TS-1E has the highest titanium content, it shows the most intense 3600 cm^{-1} band; that is, it contains a higher defective hydroxyl population. On the other hand, DR UV–Vis spectra showed that the latter sample contains a higher amount of titanium species in coordination higher-than-four (270 nm band). In conventional TS-1, such species develop by treatment of TS-1 at 80 °C with an aqueous solution of NH_4HF_2 and H_2O_2; this treatment leads to the extraction of some tetrahedral Ti sites in the form of $(NH_4)_3Ti(O_2)F_5$ [22,23]. In the present case, the use of both a TPAOH/Si ratio higher than 1 and a large amount of Ti loading (conditions met in samples TS-1D and TS-1E) may facilitate the development of this peculiar Ti species even during the synthesis of TS-1. It is worth noting that Ti loadings higher than 3, but low TPAOH/Si preparation ratios, usually lead to the additional formation of anatase and not of this peculiar Ti species.

Therefore, unlike TS-1 samples prepared by traditional methods [22,23], in the present case species absorbing at 270 nm seem not to be very reactive and should likely be assigned to partly extra-framework TiO_x species. Such a result is in agreement with the abundance of hydroxyl nests in sample TS-1E, due to the fact that not all titanium is entering the framework: such hydroxyl nests behave indeed as hydrophilic species inside channels and, therefore, they should affect the diffusion of polar molecules such as, for example, phenol formed during the reaction under study, thus increasing their residence time inside channels and therefore contributing to the decreased selectivity of the TS-1E catalyst (Fig. 8b).

Adsorption of ammonia, as followed by IR spectroscopy, showed that although TS-1E sample has the highest nominal titanium content, it does not show the most intense bands related to titanium, thus confirming that in the latter sample, in addition to framework species, titanium occurs also as less reactive extra-framework titanium oxide (also detected by DR UV–Vis spectroscopy). This not only explains the relatively low activity of TS-1E (Fig. 8a), despite the presence of both a large amount of titanium and a relatively low amount of octahedral Ti^{IV}, but also provides an interpretation for the results obtained during phenol hydroxylation. It is possible that the predominant highly coordinated Ti sites and the lower concentration of tetrahedral Ti^{IV} sites on the external of TS-1E crystallites may hinder the formation of diphenols and facilitate the formation of tar as a consecutive reaction on the BQ formed.

5. Conclusions

This work reports the identification of the reaction network in benzene hydroxylation to phenol with hydrogen peroxide, catalyzed by Titanium–silicalite (TS-1), as well as the effect of the crystallite size on the primary selectivity to phenol. Benzene is hydroxylated to phenol inside TS-1 pores, but phenol undergoes consecutive oxidation to hydroquinone; hydroquinone, however, is rapidly transformed into benzoquinone inside the restricted environment of the silicalite, before it may conterdiffuse toward the bulk liquid phase. Phenol formed on the external surface of Ti sites may undergo consecutive hydroxylation to diphenols (which are kinetically secondary products); hydroquinone, however, is not so efficiently transformed into benzoquinone as it is when formed in the TS-1 porosity. Therefore, phenol and benzoquinone are the two only kinetically primary products of benzene oxidation. Phenol may then undergo consecutive oxidation also in the bulk liquid phase by a simple thermally activated reaction. Although it is a kinetically primary product, benzoquinone is chemically consecutive to phenol; therefore, the likelihood of achieving this by-product depends on the counterdiffusion path length of phenol inside TS-1 pores. In fact, the primary selectivity to phenol, and to benzoquinone as well, was found to be a clear function of the average crystallite size of TS-1. The reactivity behavior was also affected by the solvent used, as shown in tests carried out by using different methanol-to-water ratios, in biphasic conditions. The development of a triphasic, water-rich solvent system led to a remarkable lowering of the selectivity to phenol, with the formation of large amounts of both diphenols and tar. Lastly, we produced experimental evidences that the phenol-protecting role of sulfolane co-solvent – the use of which is known to cause a higher selectivity to phenol – was different depending on the conditions used. When the solvent used inhibits the diffusion of sulfolane inside TS-1 pores, the protective effect on phenol limits the occurrence of the consecutive hydroxylation to CT and HQ. Conversely, when the conditions used facilitated the diffusion of sulfolane inside pores, the protecting effect inhibited the intracrystalline oxidation of phenol to benzoquinone.

Lastly, a modified synthesis procedure using a large excess of TPAOH allows the control of both the crystallite size of TS-1 and the nature of the Ti species. In fact, the use of high Ti/Si atomic ratios and high TPAOH/Si molar ratios led to the formation of Ti sites with Ti^{IV} sitting in coordination higher-than-four, most probably as extra-framework species. Correspondingly, a higher population of defective hydroxyls was observed: the latter species may indeed be responsible for a higher affinity of the catalysts for polar molecules, thus affecting the product distribution, with a lower initial selectivity to phenol, but did not contribute to benzene conversion.

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