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Reaction testing of phenol hydroxylation and cyclohexane oxidation by gas chromatography: influence of residual hydrogen peroxide

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Abstract

Gas chromatographic (GC) analysis and high-performance liquid chromatographic (HPLC) analysis of reaction mixtures of phenol hydroxylation on an α-Fe_2O_3 model catalyst are compared. The over-estimated phenol conversion, *para*-benzoquinone yield and *o*/*p* selectivity derived from the GC results are caused by the oxidation reactions of phenol and its hydroxylation products with hydrogen peroxide at elevated temperature in the GC system. In the GC system hydroquinone can be oxidized by a trace amount of O_2 in the N_2 carrier gas, so even in the absence of residual hydrogen peroxide the *para*-benzoquinone yield and *o*/*p* selectivity obtained might be higher than the real values. Cyclohexane, cyclohexanol and cyclohexanone are less reactive towards hydrogen peroxide at elevated temperature, so the influence of residual hydrogen peroxide on the reaction testing of cyclohexane oxidation by GC is not significant.

Keywords: Phenol hydroxylation; Cyclohexane oxidation; Hydrogen peroxide; GC analysis; HPLC analysis

1. Introduction

Catalytic oxidation processes play a key role in the manufacture of both bulk and fine chemicals [1]. Compared with gas phase oxidation, liquid phase oxidation has obvious advantages of mild reaction conditions and high activity/selectivity [2]. The commonly used oxidants are dioxygen, hydrogen peroxide and alkyl hydroperoxide, among which hydrogen peroxide is an attractive one since it is easy to handle and produces water as the co-product [3]. Over the past decades, liquid phase oxidation with hydrogen peroxide as oxidant over heterogeneous catalysts has been a fast-developing domain, particularly after the discovery of titanium silicalite (TS-1) by Enichem workers [4–8]. A variety of synthetically useful oxidations, such as olefin epoxidation, oxidation of alcohols to aldehydes, aromatic hydroxylation and ammoxidation of cyclohexanone to cyclohexanone oxime, are catalyzed by TS-1 and analogous redox zeolites or molecular sieves, including TS-2 [9], Tiβ [10], ETS-10 [11], Ti-MCM-41 [12], VS-2 [13], V-HMS [14] and Cr-APO-11 [15].

The TS-1 catalyzed hydroxylation of phenol to catechol and hydroquinone with 30% H_2O_2 has been commercialized by Enichem in the early 1990s. However, the complicated synthesis, high price and low reaction rate of the catalyst limit its wide application in industry. The search for new catalysts in this area carries on continuously the world over. Numerous reports have shown that some other vanadium, copper and iron compounds are active for phenol hydroxylation, e.g.,

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V_2O_5–SiO_2 [16], $H_xV_2Zr_2O_9{\cdot}H_2O$ [17], Cu–Bi–V–O complex [18], $CuAlCO_3$-hydrotalcite like compounds [19], $La_{2-x}Eu_xCuO_{4+\delta}$ [20], $Cu_2(OH)PO_4$ [21], Fe_2O_3/macroporous resin [22] and Fe–Mg–Si–O complex [23].

The major reaction products of phenol hydroxylation are catechol and hydroquinone, accompanied by a small amount of *para*-benzoquinone and chromatographically undetectable tar. They were analyzed either by gas chromatography (GC) or high-performance liquid chromatography (HPLC) in the literature. Comparing GC and HPLC analysis results, van der Pol et al. [24] have pointed out in a previous research letter that HPLC analysis is the preferred technique to analyze the reaction products, as long as H_2O_2 is present in the samples, because at the high temperature of the injection port and the GC column reactions between hydroquinone and catechol with H_2O_2 could be possible, while these reactions do not occur under the mild conditions of HPLC analysis. As a consequence, a relatively higher concentration of *para*-benzoquinone in the products is detected by GC, in contrast to corresponding result of the HPLC analysis. Nevertheless, GC analysis is still used in quite a lot of the later works without mentioning any special precautions [14–22,25–34].

When working on Fe-based complex oxide catalysts for phenol hydroxylation, large differences not only in results of product distribution but also in results of phenol conversion obtained by GC and HPLC analysis have been observed in our laboratory on repeated occasions. For this reason, we decided to reinvestigate the influence of residual H_2O_2 on the reaction testing by GC of the two important oxidation reactions, phenol hydroxylation and cyclohexane oxidation, more systematically and meticulously in the present work in order to obtain a more explicit picture of the problem.

2. Experimental

The chemicals, phenol (AR), hydroquinone (AR), catechol (CP) and *para*-benzoquinone (CP) were purified by vacuum distillation or sublimation and checked by HPLC. Cyclohexane (AR), cyclohexanol (AR) and cyclohexanone (AR) were checked by GC and used as obtained. 30 wt.% H_2O_2 was used as obtained.

For the preparation of α-Fe_2O_3 catalyst, 30 ml of aqueous ammonia (1:1) was placed in a three-necked flask equipped with a thermometer and a magnetic stirring bar, and 100 ml of 0.5 mol l^{-1} $Fe(NO_3)_3$ solution was added dropwise. The precipitation temperature was 50 °C and the final pH value was 9–10. After the addition, the mixture was further stirred for 30 min and aged at room temperature for 12 h. The precipitate was filtered, washed with distilled water, dried at 110 °C overnight, triturated into powder, calcined at 400 °C for 1 h, 600 °C for 2 h and then calcined at 800 °C for 4 h. The BET surface area of the catalyst was 3.1 m^2 g^{-1}.

Phenol hydroxylation was carried out at 70 °C in a three-necked flask (250 ml) equipped with a magnetic stirrer and a reflux condenser. 4.0 g phenol, 50 ml distilled water and 0.2 g catalyst were added successively into the flask. 1.4 ml of 30 wt.% H_2O_2 (PHE/H_2O_2 molar ratio = 3) was added after the mixture had been heated to 70 °C. The reaction was monitored by taking aliquots at different times. The samples were centrifugated to remove the catalyst before analysis.

An Agilent 1100 HPLC equipped with a reversed phase C18 column was used for HPLC analysis. Samples were diluted 125 times in water before analysis. The column temperature was ambient temperature and a methanol/water mixture (30/70 vol.%, 0.6 ml min^{-1}) was used as the eluant. A dual wavelength UV detector (245 and 280 nm) was employed. A Shangfen 102G gas chromatograph equipped with an on-column injector and a flame ionization detector (FID) was used for GC analysis. For analysis of phenol (PHE), catechol (CAT), hydroquinone (HQ) and *para*-benzoquinone (BQ), a fused silica capillary column (XE-60, 30 m × 0.25 mm × 0.3 μm) was used and the injector and column temperatures were 280 and 180 °C, respectively. Ethanol was used as an internal standard for water solutions and biphenyl was used as an internal standard for acetone solutions. For analysis of cyclohexane, cyclohexanol and cyclohexanone, a PEG column was used and the injector and column temperatures were 160 and 115 °C, respectively. Chlorobenzene was used as an internal standard. The conversion of the reactants and the yield of the products were calculated as follows:

$$X_R = \frac{[R]_i - [R]_f}{[R]_i} 100\%, \qquad Y_P = \frac{[P]_f}{[R]_i} 100\%$$

The subscript i and f stand for initial and final, respectively. Sample of 0.5 μl was injected for each test, and the standard deviation of GC analysis is about 2–5% depending on the concentration of the sample. The H_2O_2 concentration was determined by iodometric titration.

3. Results

3.1. Comparison of hydroxylation reaction data obtained by GC and HPLC

A comparison of the reaction data of phenol hydroxylation on α-Fe_2O_3 catalyst analyzed by HPLC and GC is shown in Fig. 1a and b. The differences between the two figures are obvious.

In Fig. 1a, nice S-shaped curves of PHE conversion, CAT yield and HQ yield are observed, showing that the reaction is slow at the beginning and accelerates after about 60 min until it reaches a plateau after 150 min. At the final stage, PHE conversion and total yield of CAT + HQ + BQ are 20.4 and 15.8%, respectively. The discrepancy between these two data is due to the formation of undetectable products during the reaction [35]. The yield of BQ is very low and the yield of CAT is consistently higher than that of HQ during the whole course of reaction. The S-shaped curves and the presence of an induction period for the reaction are associated with the free-radical reaction mechanism in liquid phase oxidation over iron oxide, which has already been discussed in our previous paper [23].

When GC is used to analyze phenol and the products instead of HPLC, the S-shaped curves disappear and the PHE conversion, CAT yield and BQ yield increase significantly at the initial stage (see Fig. 1b). The final PHE conversion is 20.8%, which is consistent with the result from HPLC, but the total product yield (13.4%) is slightly lower than that derived from the HPLC data. During the whole course of reaction, HQ yield is much lower than that in Fig. 1a, but BQ yield is increased considerably in particular before 135 min. Roughly speaking, the reaction data obtained from HPLC and GC become comparable only after it has run for more than 150 min when most of the H_2O_2 in the reaction mixture has been consumed (see Fig. 1c).

Table 1
Influence of H_2O_2 on the analysis of phenol by GC

H_2O_2 added (ml)	X_{PHE} (%)	Product yield (%)			
		Total	CAT	HQ	BQ
0	0	0	0	0	0
0.05	0	0	0	0	0
0.1	0	0	0	0	0
0.2	0	0	0	0	0
0.5	4.6	0	0	0	0
0.8	5.0	0	0	0	0
1.1	6.5	0.8	0	0	0.8
1.4	10.1	2.8	0.6	0	2.2
1.7	13.3	4.0	1.2	0.1	2.7
2.0	19.3	6.9	2.6	0.3	4.0

The above described differences in results measured by two different analysis techniques are most probably related to the occurrence of additional reactions between phenol or the products and H_2O_2 at elevated temperature in the GC system. Therefore, a series of homogeneous experiments in the absence of catalyst were designed and done as described below.

3.2. Influence of H_2O_2 on GC analysis of individual samples (PHE, CAT, HQ and BQ)

The PHE concentration in water was the same as that in the hydroxylation reaction mixture. Different amount of H_2O_2 (0.05–2.0 ml) was added into each 50 ml PHE solution immediately before GC analysis. The analysis results of the solutions are summarized in Table 1. 4.6% of PHE is converted during GC analysis when the amount of H_2O_2 added is increased to 0.5 ml. The PHE conversion is further increased with the amount of H_2O_2 added. In the meantime, BQ, CAT and HQ appear successively as reaction products, among which BQ is predominant. The total yield of CAT + HQ + BQ is always smaller than the PHE conversion, showing that quite a lot of undetectable products, e.g., tar and *ortho*-quinone, are formed. When 1.4 ml of H_2O_2 (PHE/H_2O_2 molar ratio = 3) is added, PHE conversion reaches 10.1%, which is close to the initial conversion of PHE in Fig. 1b.

Aqueous solutions of the reaction products, CAT, HQ and BQ, with various concentrations were prepared. The concentrations of the solutions were selected assuming 5–20% of the original PHE was converted to

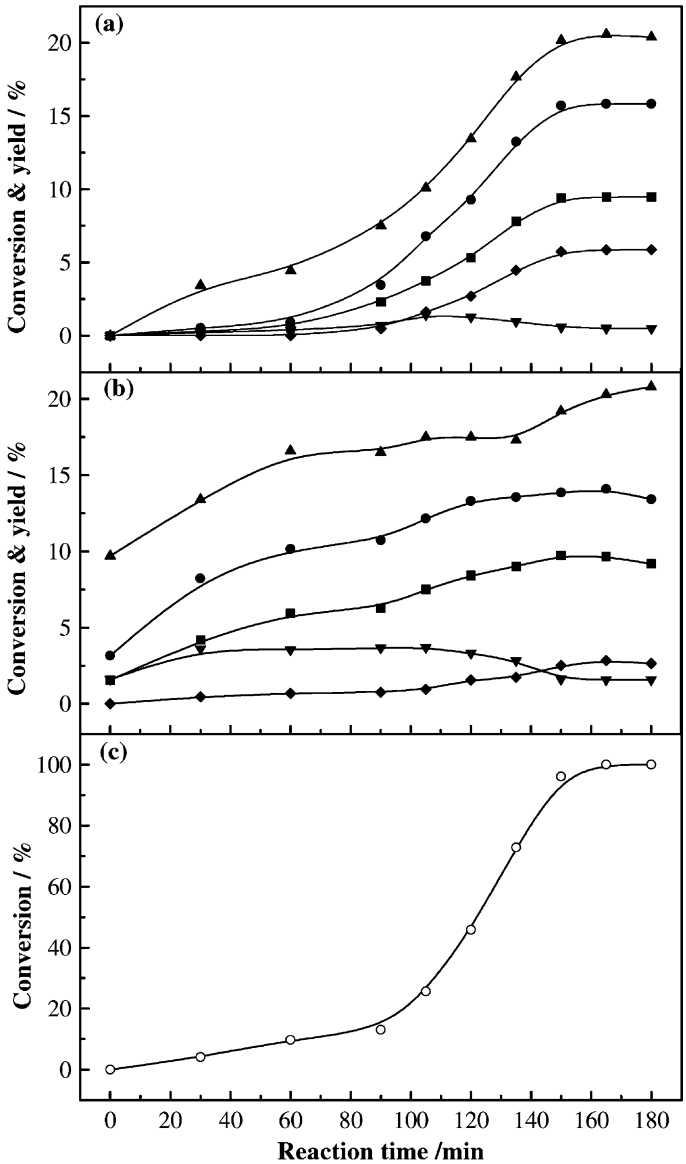

Fig. 1. Conversions of PHE (▲) and H_2O_2 (○) and yields of CAT + HQ + BQ (●), CAT (■), HQ (◆) and BQ (▼) on α-Fe_2O_3 catalyst. Reaction conditions: water as solvent; reaction temperature 70 °C; PHE/H_2O_2 molar ratio = 3; catalyst/PHE weight ratio = 0.05. Analysis by (a) HPLC, (b) GC and (c) titration.

CAT or HQ and 2–4% to BQ. Again, different amount of H_2O_2 was added into each 50 ml of solution and samples were taken and analyzed by GC. The analysis results are given in Figs. 2–4.

CAT is not reactive at low H_2O_2 concentration (see Fig. 2). A small amount of H_2O_2 (<0.1 ml) does not affect the analysis of CAT by GC. As the amount of H_2O_2 is further increased, CAT converts into undetectable products, because CAT can be oxidized with H_2O_2 at elevated temperature to form *ortho*-quinone which decomposes readily at 60–70 °C [24]. Meanwhile, CAT conversion depends on its concentration.

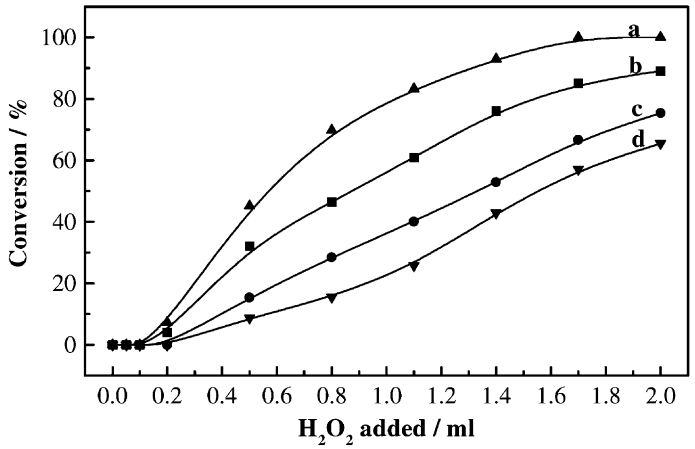

Fig. 2. Influence of H_2O_2 on the analysis of CAT by GC: (a) 0.04, (b) 0.08, (c) 0.12 and (d) 0.16 mol l^{-1}.

It increases as the solution is diluted, showing that the higher H_2O_2/CAT ratio benefits the oxidation of CAT in the GC system.

To our surprise, HQ is converted to BQ during GC analysis even in the absence of H_2O_2 (see Fig. 3). In such case, the trace amount of O_2 impurity in the N_2 carrier gas (99.998%) and the dissolved O_2 in the solution may react with HQ to form BQ in the GC system at elevated temperature. Since the amount of sample injected in each GC test is only 0.5 μl, the latter is less important than the former. Under our experimental conditions, if the contact time of HQ with N_2 is 30–60 s before the column, the O_2 in the N_2 carrier gas is stoichiometrically enough to convert HQ to the extent as shown in Fig. 3. Moreover, in Fig. 3 the conversion of HQ in the absence of H_2O_2 decreases as the concentration of HQ is increased and the stoichiometric amount of O_2 consumed for the oxidation in all the cases are close to each other, which gives a good evidence that the contact of HQ with the impure N_2 carrier gas in the GC system at elevated temperature leads to the occurrence of the oxidation reaction.

Similar to CAT conversion, the conversions of HQ and BQ increase monotonously with the amount of

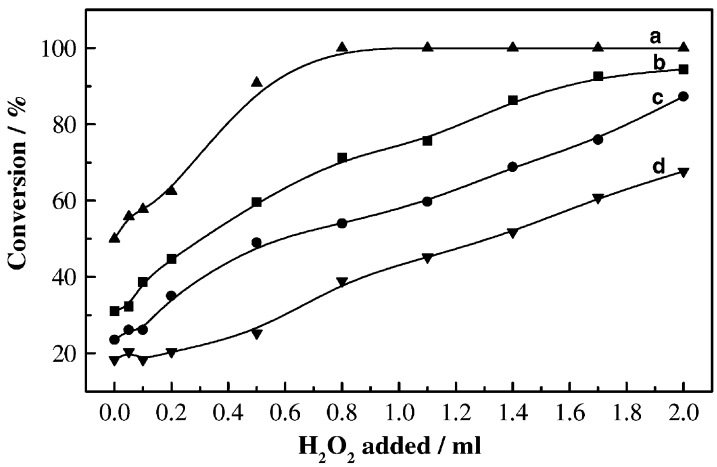

Fig. 3. Influence of H_2O_2 on the analysis of HQ by GC: (a) 0.04, (b) 0.08, (c) 0.12 and (d) 0.16 mol l^{-1}.

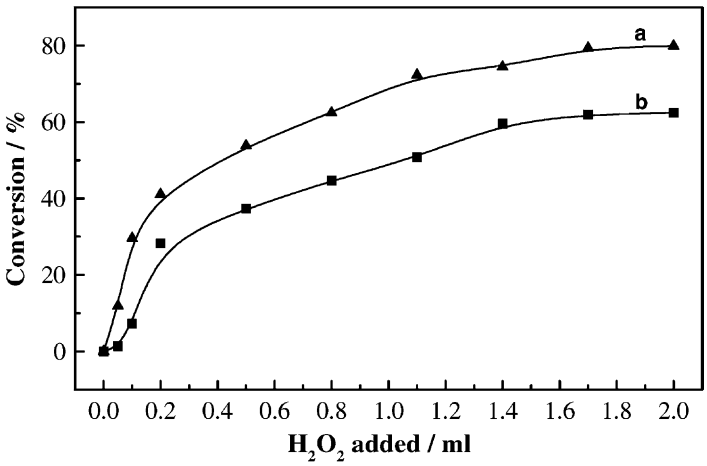

Fig. 4. Influence of H_2O_2 on the analysis of BQ by GC: (a) 0.016 and (b) 0.032 mol l^{-1}.

H_2O_2 added, and decrease as the concentration of the solutions is increased (see Figs. 3 and 4).

Representative samples were taken from the homogeneous solutions of PHE, CAT, HQ and BQ with H_2O_2 and analyzed by HPLC. The oxidation of these compounds during HPLC analysis is not observed.

3.3. Solvent effect

The above homogeneous experiments were all carried out in water solution. Since acetone is also a commonly used solvent in phenol hydroxylation, the influence of H_2O_2 on GC analysis of PHE, CAT, HQ and BQ dissolved in acetone has been investigated as well and the results are shown in Fig. 5. The variation of conversion with solvent for the reagents is different. The conversions of the PHE and BQ in acetone solution are much lower than those in water solution, whereas CAT conversion is only slightly lowered and HQ conversion is unchanged in acetone solution. The significant reduction in conversion for PHE and BQ is probably related to some change in reaction mechanism. However, solvent effect for this type of reaction is a rather complicated problem [35,36]. It is

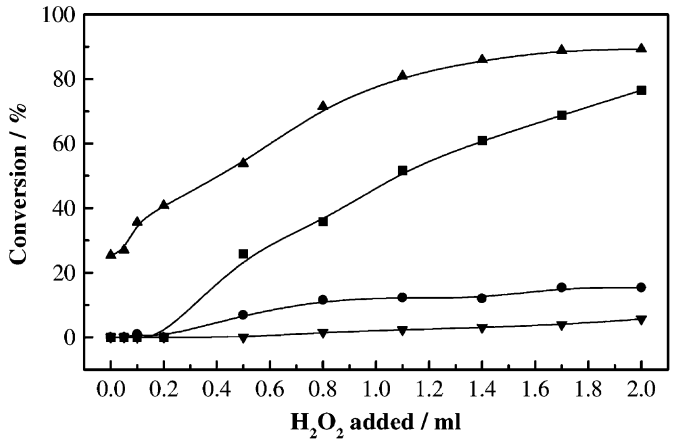

Fig. 5. Influence of H_2O_2 on GC analysis of PHE (▼), BQ (●), CAT (■) and HQ (▲) dissolved in acetone. The concentrations of PHE, CAT, HQ and BQ are 0.8, 0.08, 0.08 and 0.016 mol l^{-1}, respectively.

Table 2
Influence of H_2O_2 on GC analysis of cyclohexane, cyclohexanol and cyclohexanone in acetone solution at different injector temperatures

H_2O_2 added (ml)	Conversion (%)					
	Experiment 1 (cyclohexane)[a]	Experiment 2 (cyclohexanol)[b]	Experiment 3 (cyclohexanone)[c]	Experiment 4 (cyclohexane)[a]	Experiment 5 (cyclohexanol)[b]	Experiment 6 (cyclohexanone)[c]
0	0	0	0	0	0	0
0.2	0	0	0	0	0.5	0
0.5	0	1.4	0	0	1.6	0.8
1.0	0	3.1	1.0	0	4.5	1.6
1.5	0	3.4	2.8	0	5.1	3.1
2.0	0	3.5	3.1	0	6.5	3.3

[a] Cyclohexane:acetone = 2 ml:15 ml.
[b] Cyclohexanol:acetone = 0.2 ml:15 ml.
[c] Cyclohexanone:acetone = 0.2 ml:15 ml. Injector temperature: 160 °C (Experiments 1–3) and 250 °C (Experiments 4–6).

impossible to give an appropriate explanation for the experimental phenomenon at the moment.

3.4. Influence of H_2O_2 on GC analysis of cyclohexane, cyclohexanol and cyclohexanone

The previous experimental results show that residual H_2O_2 in the reaction mixture exerts significant influence on reaction testing of phenol hydroxylation by GC. It is worthwhile to check if this phenomenon is of common occurrence in liquid phase oxidation with H_2O_2. Cyclohexane oxidation with H_2O_2 as oxidant to form cyclohexanol and cyclohexanone is another important liquid phase oxidation reaction [37]. Redox molecular sieves, such as TS-1 [38], Ti-, V-, Cr-MCM-41 [39] and Cr-APSO-37 [40], are active catalysts for the reaction. GC analysis is often used for monitoring this catalytic oxidation reaction. In this study, six homogeneous test solutions in the absence of catalyst were injected into the GC to investigate the influence of H_2O_2 on GC analysis of these compounds, and the results are listed in Table 2.

Cyclohexane oxidation reactions are commonly carried out in acetone solution with an acetone:cyclohexane:30 wt.% H_2O_2 (volume ratio) = 15:2:2, and usually the yields of cyclohexanol and cyclohexanone are around 10%. The test solutions in Experiments 1–6 were prepared to suit these conditions.

Cyclohexane is fairly inert towards H_2O_2 in the GC system. No conversion of cyclohexane is observed in Experiments 1 and 4, regardless of the injector temperature being 160 or 250 °C. The conversions of cyclohexanol and cyclohexanone are almost negligible when the amount of H_2O_2 added is less than 0.5 ml. As the amount of H_2O_2 is increased, cyclohexanol converts to form cyclohexanone, whereas cyclohexanone is over-oxidized to form undetectable adipic acid [37,41]. Cyclohexanol is somewhat more reactive than cyclohexanone in the GC system. When 2.0 ml of H_2O_2 (simulating the initial concentration of H_2O_2 in the reaction mixture for cyclohexane oxidation) is added, the conversions of cyclohexanol and cyclohexanone are 3.5 and 3.1%, respectively, which are indeed much lower than those of the hydroxylation products of phenol. The conversions of cyclohexanol and cyclohexanone are slightly increased as the injector temperature is raised up to 250 °C.

4. Discussion

From all the previous experimental results, it may be concluded that PHE and its hydroxylation products, CAT, HQ and BQ, can react with H_2O_2 readily at elevated temperature in the GC system. An erroneous picture of the reaction may be obtained when a sufficient amount of residual H_2O_2 is present in the samples. According to the GC analysis results in this work, the sources of error can be summarized as follows:

(1) Since PHE reacts with H_2O_2 at the high temperatures of the injection port and the GC column, the PHE conversion measured by GC could be over-estimated if residual H_2O_2 is present in the sample. According to Table 1, if the initial PHE/H_2O_2 molar ratio of the reaction mixture is

Table 3
Product distribution measured by HPLC and GC for phenol hydroxylation on α-Fe_2O_3[a]

$X_{H_2O_2}$ (%)	HPLC					GC				
	X_{PHE} (%)	Y_{CAT} (%)	Y_{HQ} (%)	Y_{BQ} (%)	*o*/*p*	X_{PHE} (%)	Y_{CAT} (%)	Y_{HQ} (%)	Y_{BQ} (%)	*o*/*p*
26	10.1	3.7	1.6	1.4	2.3	17.5	7.5	1.0	3.7	7.5
46	13.4	5.3	2.7	1.3	2.0	17.5	8.4	1.6	3.3	5.3
73	17.7	7.8	4.5	1.0	1.7	17.3	9.0	1.7	2.8	5.3
100	20.6	9.5	5.9	0.5	1.6	20.3	9.7	2.8	1.6	3.5

[a] *X*—conversion and *Y*—yield. Reaction conditions: water as solvent; reaction temperature is 70 °C; PHE/H_2O_2 molar ratio = 3; catalyst/PHE weight ratio = 0.05.

3, the PHE conversion measured by GC could be +10.1, +6.5, +5.0 or +4.6% higher than the real value when H_2O_2 conversion in the reaction mixture is 0, 21, 43 or 64%, respectively. In reference to Fig. 1a–c, the difference in PHE conversion between GC and HPLC measurements is +9.7, +7.4 or +4.1% when H_2O_2 conversion in the reaction mixture is 0, 26 or 47%, respectively. These two series of results are fairly consistent. In literature [35], the optimum PHE conversion of TS-1 type catalyst is about 27%, hence the above error in measurement is definitely non-negligible, particularly in the case of searching for new catalysts or studying the reaction course.

(2) The reactivity of the hydroxylation products, CAT, HQ and BQ, towards H_2O_2 under thermal conditions varies. The results indicate that HQ is more reactive than the others. Moreover, a complex reaction network is formed, e.g. phenol reacts with H_2O_2 to form HQ, CAT and BQ, HQ reacts with H_2O_2 to form BQ, BQ reacts with H_2O_2 to form undetectable tar and CAT reacts with H_2O_2 to form *ortho*-quinone which decomposes easily in the GC system. Therefore, the product distribution measured by GC in the presence of H_2O_2 could be distorted. The product distribution at different H_2O_2 conversion levels measured by HPLC and GC for phenol hydroxylation on α-Fe_2O_3 catalyst was calculated and listed in Table 3. It is obvious that the lower the H_2O_2 conversion (i.e. the more residual H_2O_2 in the sample) the larger the discrepancy between the data from the two analysis techniques. Both the yield of BQ and the *o*/*p* ratio (CAT/HQ ratio) measured by GC are twofold to threefold higher than the real values due to the high reactivity of HQ with H_2O_2 in the GC system. At the end of the reaction, H_2O_2 is completely consumed and the PHE conversions obtained by the two techniques coincide. However, the BQ yield and *o*/*p* ratio measured by GC are still higher due to the oxidation of HQ with the oxygen in the N_2 carrier gas. This kind of error might be avoided if purer N_2 with less that 0.001% O_2 is used as the carrier gas in the GC system.

(3) Solvent effect has been observed in the reaction of PHE and its hydroxylation products with H_2O_2 under thermal conditions. According to Fig. 5, PHE and BQ conversions decrease significantly in acetone solution, whereas CAT conversion is slightly lowered and HQ conversion is unchanged in acetone solution. Hence, when phenol hydroxylation is performed in acetone instead of water, the error in measurement of PHE conversion by GC may be reduced. However, the distortion in product distribution does still exist due to the high reactivity of HQ and CAT with H_2O_2 in the GC system.

The previous arguments confirm that HPLC is the preferred technique for reaction testing of phenol hydroxylation as long as H_2O_2 is present in the reaction mixture because of the high reactivity of PHE, HQ, CAT and BQ with H_2O_2 in the GC system. Fortunately, the injector and column temperatures for analysis of cyclohexane, cyclohexanol and cyclohexanone are lower, and cyclohexane is inert to H_2O_2 at these temperatures. Hence, the conversion of cyclohexane in its oxidation reaction measured by GC is unaffected by the residual H_2O_2 in the reaction mixture. H_2O_2 does react with cyclohexanol in the GC system to form cyclohexanone and react with

cyclohexanone to form gas chromatographically undetectable products such as adipic acid, but the reactivities of cyclohexanol and cyclohexanone are rather low in comparison to phenol and its hydroxylation products. According to Table 2, the conversions of cyclohexanol and cyclohexanone are only 3.5 and 3.1%, respectively, even when the H_2O_2 concentration in the samples is set to be as high as its initial concentration in the reaction mixture. Such a small error is acceptable in catalytic testing. Therefore, GC can be considered as a safe analysis technique for cyclohexane oxidation.

5. Conclusions

For the hydroxylation of phenol with H_2O_2, large differences have been observed between GC and HPLC analysis results. Using GC for the analysis of reaction mixtures in the presence of residual H_2O_2, PHE conversion is over-estimated and BQ yield and *o*/*p* ratio of the products are twofold to threefold higher than the real values, because PHE, HQ, CAT and BQ are oxidized by H_2O_2 at elevated temperature in the GC system. Oxygen impurity in the N_2 carrier gas is another factor worthy to be considered. In the GC system, HQ can be oxidized by a trace amount of O_2 in the carrier gas, leading to an unreal increase in BQ yield and *o*/*p* selectivity even in the absence of H_2O_2. Hence, HPLC is the preferred technique for the reaction testing of phenol hydroxylation.

Cyclohexane is inert to H_2O_2 at elevated temperature, whereas the products of cyclohexane oxidation, cyclohexanol and cyclohexanone, are much less reactive with H_2O_2 than phenol, hydroquinone, catechol and *para*-benzoquinone. The influence of residual H_2O_2 on the reaction testing of cyclohexane oxidation with H_2O_2 by GC is not as important as that of phenol hydroxylation.

Acknowledgements

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