

Review

One-Step Catalytic or Photocatalytic Oxidation of Benzene to Phenol: Possible Alternative Routes for Phenol Synthesis?

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Abstract: Phenol is an important chemical compound since it is a precursor of the industrial production of many materials and useful compounds. Nowadays, phenol is industrially produced from benzene by the multi-step “cumene process”, which is energy consuming due to high temperature and high pressure. Moreover, in the “cumene process”, the highly explosive cumene hydroperoxide is produced as an intermediate. To overcome these disadvantages, it would be useful to develop green alternatives for the synthesis of phenol that are more efficient and environmentally benign. In this regard, great interest is devoted to processes in which the one-step oxidation of benzene to phenol is achieved, thanks to the use of suitable catalysts and oxidant species. This review article discusses the direct oxidation of benzene to phenol in the liquid phase using different catalyst formulations, including homogeneous and heterogeneous catalysts and photocatalysts, and focuses on the reaction mechanisms involved in the selective conversion of benzene to phenol in the liquid phase.

Keywords: benzene; phenol; selective oxidation; homogeneous (photo)catalysts; heterogeneous (photo)catalysts

1. Introduction

Phenol (hydroxybenzene) was discovered in coal tar and, under ambient conditions, appears as a white crystalline solid with a characteristic odor. It is an important industrial commodity, typically obtained from benzene. The use of phenol has been increasing due to its importance as a raw material from which to obtain other products [1]. The conversion of benzene to phenol possesses great relevance since phenol is a solvent and an intermediate of other kinds of industrial production, being a precursor of many materials and useful compounds [1]. Some examples of the usage of phenol are reported in the following:

- (1) PHENOLIC RESINS: by the reaction of phenol or substituted phenol with formaldehyde, phenol–formaldehyde resins or phenolic resins can be obtained. The first example was Bakelite as a commercial synthetic resin [2].
- (2) POLYCARBONATES (a very pure phenol feed is required): polycarbonates are thermoplastic polymers containing carbonate groups in their chains [3].
- (3) EPOXY RESINS: epoxy phenolic resins are resins modified at the phenolic hydroxyl group to include an epoxide functional group. This addition increases the ability of the resin to crosslink, creating a stronger polymer [4].

- (4) **INTERMEDIATE FOR CAPROLACTAM** (nylon production): caprolactam is a monomer for nylon production. Among the routes for its manufacture, one is via cyclohexanone and cyclohexanone oxime. Cyclohexanone can be prepared either from phenol or from cyclohexane. The phenol route is a two-stage process, in which the first stage foresees the reaction among phenol and hydrogen in the presence of a nickel catalyst at around 180 °C to form cyclohexanol, subsequently dehydrogenated at around 400 °C in the presence of a copper catalyst to yield the cyclohexanone [5].

The cumene process (also known as the Hock process) is the most important industrial process for the simultaneous production of phenol and acetone starting from benzene and propylene [6]. Oxygen from air and small amounts of a radical initiator are also reactants required for the process. The cumene process is very complex, as it consists of several stages, passing through the formation of hydroperoxide (a very reactive substance that can give runaway phenomena), which allows the indirect production of phenol and acetone [7]. The process has three main reaction steps plus, furthermore, a step of concentration of cumene hydroperoxide, and they are as follows: (i) production of cumene; (ii) conversion of cumene to cumene hydroperoxide; (iii) concentration of cumene hydroperoxide; (iv) hydrolysis of cumene hydroperoxide [1].

The scheme of the reactions is reported in Figure 1.

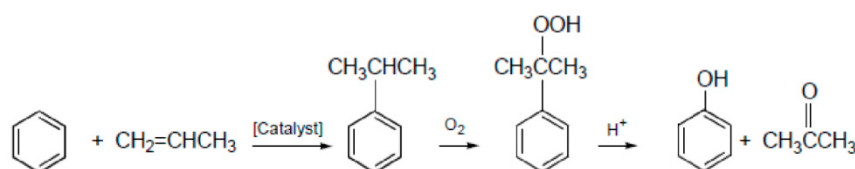


Figure 1. The reaction steps for phenol production via the cumene process.

The production of cumene (isopropylbenzene) is a Friedel–Crafts reaction and occurs by the reaction between benzene and propene, using an acid catalyst [8].

In one process, benzene and propene (3:1 mole ratio) are passed over an acid catalyst. The excess benzene acts to limit the polyalkylations and the by-reactions of the oligomerization of propene. The zeolite is more environmentally friendly than traditional acid catalysts. The problems are related to selectivity because isomers can be produced with respect to cumene [8].

The second step, the conversion of cumene to cumene hydroperoxide, involves the use of air to give the hydroperoxide in the presence of small quantities of a radical initiator (benzoyl peroxide, for example) in slightly basic conditions.

The reaction is autocatalyzed by cumene hydroperoxide. The reaction is carried out at temperatures between 77 and 117 °C and 1–7 atm pressure, to hold the system in the liquid phase.

After the concentration of the cumene hydroperoxide, performed usually with an evaporator at the descendent film, the third and final reaction is the decomposition of cumene hydroperoxide by mixing with sulfuric acid at 40–100 °C to give, after neutralization, phenol and propanone (acetone). Then, the products are separated through distillation columns.

The economics and effectiveness of this process are related to the market of acetone, apart from phenol. Often, much more phenol is needed than the propanone that is produced at the same time. Moreover, this multistage process has a low overall yield (less than 5%), requires high energy, and the formation of by-products such as acetophenone, 2-phenylpropan-2-ol, and α -methylstyrene is encountered [9].

Today, almost 95% of the worldwide phenol production is based on the “cumene process”, despite the previously mentioned drawbacks, which are poor ecology, the formation of an explosive intermediate (cumene hydroperoxide), high capital investment, high acetone production as a co-product, which results in an oversupply in the market, and a multistep characteristic which makes it difficult to achieve high phenol yields with respect to benzene feed [10]. Therefore, it is highly desirable to develop alternative synthetic processes of phenol which are more efficient and environmentally benign.

In fact, in this regard, great interest is devoted to the process in which the direct oxidation of benzene to phenol is achieved, thanks to the use of suitable catalysts and oxidant species.

Therefore, this review aims to summarize the catalytic and photocatalytic formulations studied to date for the direct conversion of benzene to phenol in the liquid phase. It is worthwhile to note that, to the best of our knowledge, only a few review articles on this topic, mainly devoted to the role of oxidant molecules (O_2 or H_2O_2) [11,12], to the use of molecular sieves [13], and to the use of nano-biomimetic metal oxide catalysts [14], are present in the literature. Additionally, until now, no review which summarizes photocatalyst formulations suitable for the direct oxidation of benzene to phenol in the liquid phase has been developed.

2. Homogeneous and Heterogeneous Catalysts for the One-Step Catalytic Oxidation of Benzene to Phenol in Liquid Phase

As highlighted above, the development of a process able to synthesize phenol from benzene in a one-step reaction with high benzene conversion and high phenol selectivity is highly desired, both from environmental safety and economical points of view [11].

Theoretically, the high conversion of benzene to phenol through oxidation reactions (Figure 2) is possible, but the experimental results evidence that this goal is difficult to achieve. The more investigated process is the direct hydroxylation of benzene using N_2O [15], O_2 [16], H_2O_2 [17,18], and a mixture of O_2 and H_2 [19] as oxidant species.

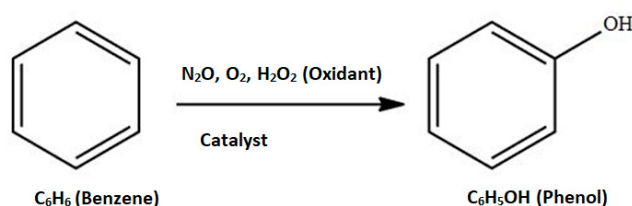


Figure 2. One-step catalytic oxidation of benzene to phenol using different oxidants.

In all cases, the thermodynamic analysis (carried out utilizing the data reported in Table 1) indicates that the reaction is irreversible and 100% conversion is feasible.

Table 1. Standard heat of reaction (ΔH°) and standard Gibbs free energy (ΔG°) for benzene, phenol, and for the different oxidant species.

	Component	ΔH° at 298 K (kJ/mol)	ΔG° at 298 K (kJ/mol)
Reagent	Benzene (l)	48.99464	124.34848
	Benzene (g)	82.92688	129.66216
Oxidant	H_2O_2 (l)	−136.10552	−105.47864
	N_2O (g)	82.04824	104.1816
	O_2 (g)		
	H_2 (g)		
Product	Phenol (s)	−165.01696	−50.4172
	Phenol (g)	−96.35752	−32.88624
	H_2O	−285.82996	−237.178408

In particular, high selectivity to phenol could be achieved using N_2O as oxidant, but high reaction temperature is required and sources of N_2O are limited. On the other hand, air or oxygen is easily available. Among the oxidant agents, hydrogen peroxide is the most considered oxidant since water is the only by-product and the process is simple, green, and economic [13]. On the other hand,

the hydroxylation reaction of benzene with the presence of only the oxidant is very slow and not able to oxidize benzene into phenol [20].

For this reason, to develop this process, it is essential to identify the right catalyst capable of guaranteeing high selectivity to phenol together with a high conversion of benzene. The main driving force of the development of new, efficient oxygenation catalysts is to selectively hydroxylate the non-activated C–H bonds of the benzene molecule in order to reduce the steps required in the preparation of phenol [21]. However, the direct introduction of hydroxyl into the benzene molecule is very difficult because of the low reactivity of aromatic C–H bonds and the strong nucleophilicity of hydroxyl free radicals [22]. Additionally, phenol is more reactive than benzene, resulting in further oxidation reactions of phenol and, consequently, the selectivity worsens [23], as also recently underlined in a paper dealing with the catalytic conversion of benzene to p-benzoquinone [24]. Therefore, the formulation of effective catalysts for phenol production, with a good yield and a high selectivity to the desired product, is highly desirable.

Numerous homogeneous catalysts have been tested [25–27], such as high active Co complexes [28], Ni complexes [29], Cu-based complexes [30–34], as well as nitrogen- [35,36] or oxygen-ligated [37,38] iron complexes. Additionally, Os complexes were discussed as non-trivial catalysts for benzene oxidation (oxidation with $\text{H}_2^{16}\text{O}_2$ under $^{18}\text{O}_2$ gave phenol that did not contain the ^{18}O isotope), pointing out “Os=O” as oxidizing species responsible for phenol formation [39].

Very interesting results were reported using ionic liquids with hydrogen peroxide as oxidant and ferric tri (dodecanesulfonate) as a catalyst in an aqueous solution [25]. In particular, thanks to the presence of 1-n-octyl-3-methylimidazolium tetrafluoroborate as an ionic liquid, enhanced benzene conversion (54%) together with significant phenol selectivity (90%) were observed after 6 h and at a reaction temperature of 50 °C. Additionally, the authors showed that, in the absence of ionic liquid, lower conversion and selectivity were achieved because of the formation of hydroquinone and biphenyl as by-products, underlining that the aqueous–ionic liquid biphasic reaction system is able to enhance both the benzene conversion and phenol selectivity [25]. Moreover, it was underlined that the ionic liquid containing the catalyst may be separated from the products in the aqueous phase by a simple decantation step [25].

$\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ polyoxometalate (POM) as a homogeneous catalyst is able to oxidize benzene to phenol at room temperature in the presence of only O_2 as the oxidant molecule at 170 °C for 6 h [40]. With these operating conditions, hydroxylation to phenol took place. However, they underlined that the oxidation of benzene is possible even at room temperature and that phenol can be formed thanks to the formation of a benzene radicaloid species (Figure 3) in the presence of H_2SO_4 aqueous solution via an electron transfer mechanism and the subsequent oxidation reaction promoted by O_2 present in the reaction medium [40].

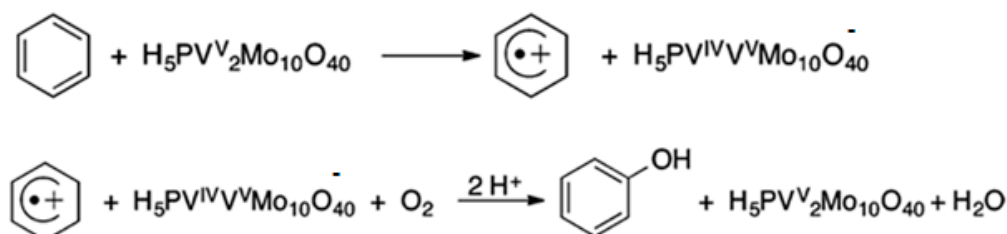


Figure 3. Oxidation of benzene to phenol using POM in the presence of H_2SO_4 aqueous solution and O_2 as oxidant. Adapted with permission from [40]. Copyright (2016) American Chemical Society.

Amphiphilic poly(ionic liquid) (PIL)/Wells–Dawson-type phosphovanadomolybdate (V-POM) ionic composites were also studied in benzene hydroxylation with H_2O_2 , showing a phenol yield of 37.3% with a selectivity of 100% [41].

Other interesting homogeneous catalysts for the hydroxylation of benzene to phenol are a series of first-row transition metal complexes with Schiff base ligands or with readily available acetylacetonate ligands, which were studied for the hydroxylation of benzene to phenol at 50 °C in acetonitrile, using hydrogen peroxide as the oxidant [42]. In this context, Fe(II) complex with the N4 Schiff base ligand allowed the achievement of phenol selectivity and benzene conversion equal to 98% and 64%, respectively [42]. On the other hand, Fe(II) and Fe(III) acetylacetonate complexes evidenced 96% selectivity to phenol, but with a lower benzene conversion (20–22%). Therefore, the reported results evidenced that phenol was the main reaction product, without the formation of biphenyl as a by-product, suggesting that the reaction does not take place through a free radical mechanism [36].

A solution different to homogeneous catalysis is based on the development of solid catalysts, which offer more efficiency together with high stability under the reaction conditions. Heterogeneous catalysts, if compared to homogeneous catalysts, have some advantages, such as catalyst recovery and recycling, which is the primary goal in view of the possible industrialization of the process. Different studies deal with the oxidation of benzene to phenol by using a transition metal oxide (such as Ti, V, Mn, Fe, Co, Cr, Mo) supported on a different metal oxide (such as Al₂O₃, SiO₂, and TiO₂). Among them, it was reported that vanadium-based compounds exhibited excellent catalytic activity towards the hydroxylation of benzene to phenol [43]. For example, as reported in Table 2, Shijina et al. analyzed the oxidation reaction carried out over supported vanadia. The experimental results evidenced that, at 60 °C, the activity increases, with an increase in vanadia content up to 13.8%. After monolayer dispersion, i.e., above 14% V₂O₅, the percentage conversion of benzene decreased [44]. However, the weak interaction of V and support leads to the leaching of active phases from the support [45]. Furthermore, for example, in the case of vanadium supported on Al₂O₃, the presence of stable V₂O₅ disfavors the redox cycle between V⁵⁺ and V⁴⁺ [46], reflected in the low catalytic activity.

Table 2. Main catalytic formulations for the one-step catalytic oxidation of benzene to phenol in liquid phase.

Catalyst	t (h)	T (°C)	P (atm)	Operating Conditions	Benzene Conversion (%) X	Phenol Yield (%) η	Selectivity to Phenol (%) S_p	Ref.
CuO/Al ₂ O ₃	-	80	1	80 vol% acetic acid; benzene: 22.5 mmol; ascorbic acid: 4 mmol.	-	1.2	-	[47]
V/Al ₂ O ₃	-	30	4	80 vol% acetic acid; benzene: 5.6 mmol; ascorbic acid: 1 mmol.	-	8.4	-	[48]
V ₂ O ₅ -Al ₂ O ₃	6	60	1	Catalyst: 0.2 g (14 wt% V ₂ O ₅); benzene: 1.46 mmol; acetonitrile: 4 mL; H ₂ O ₂ : 11.68 mmol.	13	-	100	[44]
Fe ³⁺ -Al ₂ O ₃	6	60	1	Catalyst: 0.20 g; acetonitrile: 4 mL; benzene: 1.24 mmol; H ₂ O ₂ : 6 mmol.	12	12	-	[21]
Ru/SiO ₂ Rh/SiO ₂ Pd/SiO ₂ Ir/SiO ₂ Pt/SiO ₂	-	20	1	Catalyst: 0.5 wt.-% metal/SiO ₂ : 1.0 g; H ₂ /O ₂ = 3; benzene: 20 mL; acetic acid: 25 mL.	-	-	0 99.7 88.2 64.5 63.9	[49]
Ru/SiO ₂ Rh/SiO ₂ Pd/SiO ₂ Ir/SiO ₂ Pt/SiO ₂	-	60	1	Catalyst: 0.5 wt.-%; metal: 20wt.-%; V ₂ O ₅ /SiO ₂ : 1.0 g; H ₂ /O ₂ : 3; benzene: 20 mL; acetic acid: 25 mL.	-	-	100 100 99.7 100 100	[49]
0.1%V/SiO ₂	-	70	1	Catalyst: 0.204 g; benzene: 40 mmol; benzene/H ₂ O ₂ mole ratio: 1; acetonitrile: - mL.	10	-	81	[50]
Fe ₅ V _{2.5} Cu _{2.5} /TiO ₂	4	30	1	Catalyst: 0.2 g; benzene: 11 mL; benzene/H ₂ O ₂ mole ratio: 0.5; acetonitrile: 40 mL.	9.8	7.154	73	[51]

Table 2. Cont.

Catalyst	t (h)	T (°C)	P (atm)	Operating Conditions	Benzene Conversion (%) X	Phenol Yield (%) η	Selectivity to Phenol (%) S_p	Ref.
FePt/TiO ₂ (5%;1%)	4	30	1	Catalyst: 0.2 g; benzene: 11 mL; benzene/H ₂ O ₂ mole ratio: 0.5; acetonitrile: 40 mL.	6.5	5.92	91	[52]
V/MCM-41 [Si/V = 1/9.4]	6	60	1	Catalyst: 0.05 g; benzene: 6 mL; benzene/H ₂ O ₂ mole ratio: 1/1.15; acid acetic: 6 mL.	1.4	-	93	[53]
4%Cu/MCM-41	1.6	30	1	Catalyst: 0.05 g; benzene: 1 mL; benzene/H ₂ O ₂ mole ratio: 1/2; acid acetic: 7.5 mL.	21	19.7	94	[18]
Ti-MCM-41 [Si/Ti = 25]	3.5	65	1	Catalyst: 0.05 g; benzene: 0.045 mol; benzene/H ₂ O ₂ mole ratio: 1/3; acetone: 15 g.	98	-	>95	[54]
VO _x /FeSBA-15 VO _x /CoSBA-15 VO _x /NiSBA-15 VO _x /CrSBA-15 VO _x /MnSBA-15 VO _x /ZnSBA-15 VO _x /AgSBA-15 VO _x /CuSBA-15	5	80	1	Catalyst: 0.05 g; benzene: 1 mL; solvent (acetic acid/H ₂ O v/v): 36 mL; ascorbic acid: 11.9 mmol.	-	12.8 11.3 15.8 10.2 17.2 17.9 18.1 24.7	-	[55]
Fe/SBA-16	8	65	1	Catalyst: 0.1 g; benzene: 1 mL; H ₂ O ₂ : 2 mL; acetonitrile: 20 mL;	12.1	11.7	96.4	[56]
1.4wt%Cu(II)-N	6	70	1	Catalyst: 0.025 g; benzene: 0.02 mol; H ₂ O ₂ : 0.02 mol.	33.2	-	100	[57]
Graphene (CCG)	16	60	1	Catalyst: 0.02 g; benzene: 130 mg; H ₂ O ₂ : 2.4 mL; acetonitrile: 1.2 mL.	17.8	17	> 99	[58]
4.2V/NC-600	3	70	1	Catalyst: 0.02 g; benzene: 0.4 mL; H ₂ O ₂ : 1.4 mL; acetic acid: 5 mL.	27.7	26.8	96.7	[59]
4V/MCN-S	3	70	1	Catalyst: 0.02 g; benzene: 0.4 mL; H ₂ O ₂ : 1.4 mL; acetic acid: 5 mL.	38.2	36.7	96.1	[60]
Fe ₃ O ₄ /CMK-3	4	60	1	Catalyst: 0.02 g; benzene: 1 mL; H ₂ O ₂ : 2 mL; acetonitrile: 6 mL.	18	-	92	[61]
10V/mp-C ₃ N ₄	3	60	1	Catalyst: 0.06 g; benzene: 1.5 mL; H ₂ O ₂ : 3 mL; acetonitrile: 6 mL.	18	18	93	[62]
Ce _{0.07-0.07} V-g-C	4	70		Catalyst: 0.04 g; benzene: 1 mL; H ₂ O ₂ : 3.5 mL; acid acetic: 10 mL.	33.7	32.3	95.9	[63]
Cr/g-C ₃ N ₄ -300	7	65		Catalyst: 0.04 g; benzene: 3.36 mmol; H ₂ O ₂ : 1.2 mL; acetonitrile: 2 mL.	31.1	30.9	99.5	[64]
FeCl ₃ /eg-C ₃ N ₄	3	60	1	Catalyst: 0.05 g; benzene: 11.2 mmol; H ₂ O ₂ : 3 mL; acetonitrile: 5 mL.	22	22	99	[65]
Fe-TBAPy	3	60	1	Catalyst: 0.05 g; benzene: 11.2 mmol; H ₂ O ₂ : 3 mL; acetonitrile: 5 mL.	-	64.5	92.9	[66]
Cu-SA/HCNS	12	60		Catalyst: 0.05 g; benzene: 0.4 mL; H ₂ O ₂ : 6 mL; acetonitrile: 6 mL.	86	-	96.7	[67]

Molecular sieves (such as MCM-41, SBA15, SBA16, NaY) with incorporated transition metals have attracted much interest because of the high catalytic activity for the oxidation of organic compounds, such as benzene. Moreover, in this case, the presence of heteroatoms (such as V, Cu, and Fe) in molecular sieves is able to modify the surface properties so as to obtain highly dispersed and isolated active sites in the silica framework and, therefore, improving the catalytic activity. Figure 4 presents the mechanism suggested by Jourshabani et al. [56] over Fe-SBA16. The authors suggested that, compared with other Fe-based catalysts, the high catalytic activity of the systems may be attributed to SBA-16, which allows a guaranteed high mass transfer rate of benzene on the Fe/SBA-16 surface.

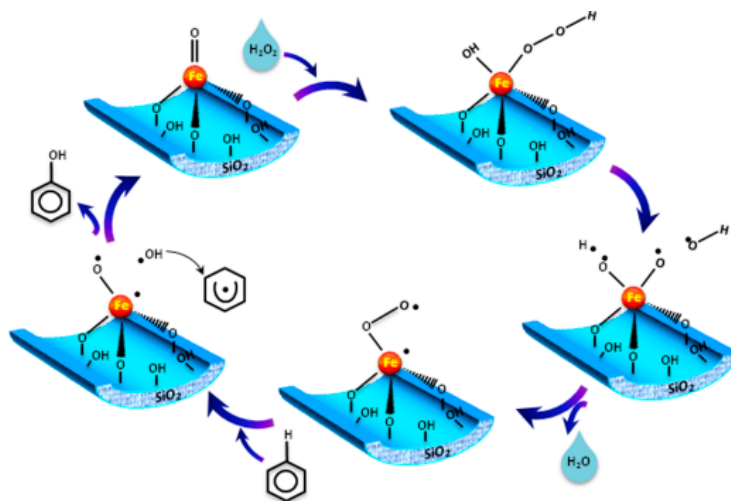


Figure 4. Proposed reaction mechanism for phenol production in the presence of Fe/SBA-16. Reprinted with permission from [56]. Copyright (2016) American Chemical Society.

In detail, the authors proposed a reaction mechanism using H_2O_2 in the presence of Fe/SBA-16, underlining that only isolated species of Fe^{3+} are the active phases. H_2O_2 is activated on Fe/SBA-16 by chemisorption on the surface of the supported Fe, together with the formation of an open bi-radical form of the iron–peroxo complex. These radicals may coordinate to Fe present in Fe/SBA-16, forming an iron–peroxo complex. Similarly, a mechanism was proposed by Hu et al. [59] using vanadium-containing nitrogen-doped mesoporous carbon catalysts. Moreover, the same authors reported a further increase in phenol yield using carbon materials as the active phase for vanadium. Carbon materials, due to their high specific area, large pore volume, and hydrophobic surface properties, represent promising supports for the hydroxylation of benzene to phenol [60]. In particular, the 4V/MCN-S catalyst (Table 2) exhibited remarkable catalytic performance, with a benzene conversion of 38.2% and phenol selectivity of 96.1%, along with good reusability. Recently, as reported in Table 2, metal-doped carbon nitride [62–65] showed improved activity for the hydroxylation of benzene with H_2O_2 to phenol but remains unsatisfactory since phenol is further oxidized, forming other by-products [13].

On the contrary, different results were obtained by Tu et al., who synthesized by the solvothermal method an Fe-based metal-organic framework (MOF) named Fe-TBAPy (Figure 5).

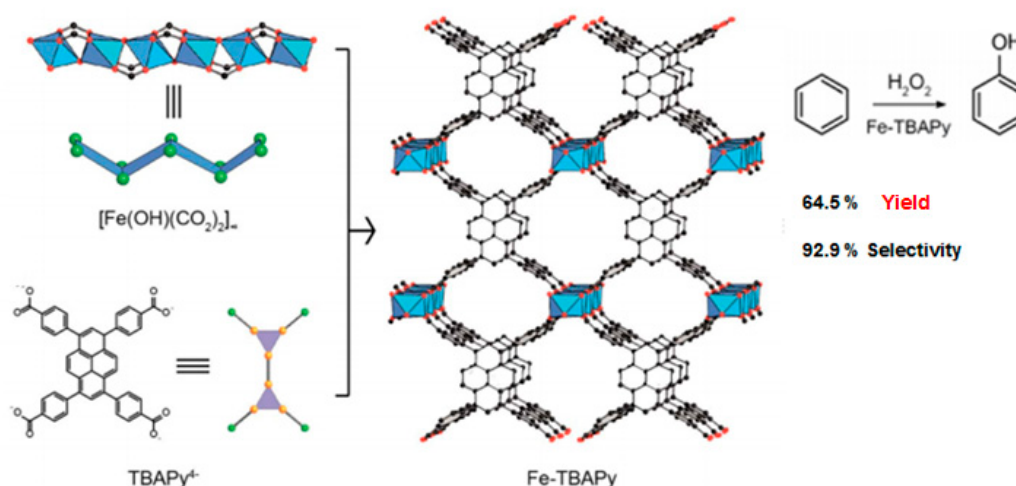


Figure 5. Mechanism of catalytic benzene hydroxylation by H_2O_2 in the presence of Fe-TBAPy [66]. Published by The Royal Society of Chemistry.

Fe-TBAPy is built from $[\text{Fe}(\text{OH})(\text{CO}_2)_2]_\infty$ rod-shaped SBUs (SBUs = secondary building units) and 1,3,6,8-tetrakis(p-benzoate)pyrene (TBAPy^{4-}). The experimental tests evidenced a high phenol yield and selectivity equal to 64.5% and 92.9%, respectively. These results demonstrated the possibility to formulate MOFs possessing enhanced catalytic activity for benzene hydroxylation. However, even if, in the last few years, significant progress has been achieved, the catalytic performance is still limited by the intrinsic drawbacks of the employed catalysts. For example, the hydrophilicity of the catalyst's surface worsens the adsorption of non-polar benzene on its surfaces and, on the contrary, favors the adsorption of polar phenol molecules, with consequently low benzene conversion and poor phenol selectivity [17]. Moreover, in some cases, the leaching of active species during the reaction is one of the main causes of deactivation of the catalyst [68].

3. Homogeneous and Heterogeneous Photocatalysts for the One-Step Catalytic Oxidation of Benzene to Phenol in Liquid Phase

The selective hydroxylation of benzene to phenol by means of photocatalysis using different oxidizing agents including O_2 [69], N_2O [70], or H_2O_2 [71] was the object of several research papers.

For this purpose, both homogeneous and heterogeneous photocatalysts were studied, although the latter evidenced some drawbacks. More specifically, in a homogeneous system, it is difficult to separate the catalyst from the reaction products [72]. In the case of homogeneous systems, Fenton's reaction is a well-known homogeneous oxidation process in which Fe^{2+} is used as a catalyst and hydrogen peroxide as oxidant [73]. However, this process requires acidic conditions that lead to corrosion phenomena [74], and also more than 40% of the used hydrogen peroxide is consumed by side reactions [75].

Moreover, the literature reported the selective oxygenation of benzene to phenol with an oxygen-saturated acetonitrile solution containing benzene water and at ambient conditions using 3-cyano-1-methylquinolinium ion (QuCN^+) as a homogeneous photocatalyst, showing a strong oxidizing ability towards benzene [76]. The hydroxylation of benzene to phenol under UV irradiation was also studied using alkoxohexavanadate anions and quinolinium ions, achieving high phenol selectivity (>99%) together with a good yield (around 50%) [77].

As an alternative to homogeneous photocatalysis, the heterogeneous photocatalytic process could represent a possible green alternative for selective oxidation reactions [78–83]. Among the semiconductor photocatalysts, TiO_2 is the most used material because of its chemical stability and its high oxidizing ability. It has been reported that the crystalline anatase phase of TiO_2 has higher photocatalytic activity, if compared to rutile TiO_2 , because the anatase phase has higher levels of hydroxyl groups on its surface [84]. The anatase TiO_2 presents a wide band gap of 3.2 eV and it is

normally activated under ultraviolet (UV) light [85,86]. When a TiO₂ photocatalyst is irradiated with energy greater than the TiO₂ band gap energy, positive charge-holes are generated in the valence band, while the electrons are promoted in the conduction band. Both positive holes and electrons take part in oxidation–reduction reactions. In particular, the photogenerated positive hole is able to react with adsorbed water to produce hydroxyl radicals, whereas the electron can reduce O₂, generating strongly oxidizing superoxide ions. These highly reactive species, such as hydroxyl radicals, are employed for phenol production from benzene under mild conditions through the photocatalytic process [87].

Table 3 reports some photocatalytic systems studied in the literature for the direct oxidation of benzene to phenol in the liquid phase.

Table 3. Main photocatalytic formulations for the one-step catalytic oxidation of benzene to phenol in liquid phase.

Photocatalyst	t * (h)	Light Source	Operating Conditions	Benzene Conversion (%) X	Phenol Yield (%) η	Selectivity to Phenol (%) S _p	Ref.
nTiO ₂ mTiO ₂ mTiO ₂	2 2 6	Hg lamp λ > 320 nm	Photocatalyst: 10 mg + nitrogen flow H ₂ O: 10 mL benzene: 20 μmol pH 7	26 23 42	2 19 34	8 83 81	[88]
TiO ₂	6	450 W Xe arc lamp	Photocatalyst: 25 mg Benzene: 20 mM [Fe ³⁺]: 1.47 mM [Ag ⁺]: 0.98 mM H ₂ O ₂ : 9.4 mM	-	<1	96	[9]
Pt-TiO ₂	1.5	λ > 385 nm	Photocatalyst: 0.2 g benzene: 0.05 mL H ₂ O: 4 mL	-	2.1	91	[89]
Au-P25: in 100 kPa air in 230 kPa CO ₂ P25: in 100 kPa air in 230 kPa CO ₂	24	Solar simulator	Photocatalyst: 60 mg aqueous benzene solution: 20 mL C ₀ benzene: 600 ppm dry ice: 0–200 mg closed container: 50 mL	13 14 34 31	8 13 7 7	62 89 21 22	[90]
Au-V-TiO ₂	18	400 W Hg lamp λ = 200–400 nm	Photocatalyst: 30 mg CH ₃ CN: 2 mL benzene: 1 mL (25 wt%) H ₂ O ₂ : 2 mL	18	16	88	[86]
Pt/WO ₃ -K	^a 1 ^b 4 ^c 0.25	300 W Xe lamp λ > 300 nm ^c λ > 400 nm	Photocatalyst: 50 mg C ₀ benzene: 2.5 mmol L ⁻¹ H ₂ O: 7.5 mL 279 K O ₂ ^d Ar	{ 22.2 ^a 68.9 ^b	{ 79.3 ^a 73.7 ^b	{ 79.3 ^a 73.7 ^b	[91]
Pt/WO ₃ -K				{ 26.6 ^{a, c} 52.5 ^{b, c}	{ 83.8 ^{a, c} 75.1 ^{b, c}	{ 83.8 ^{a, c} 75.1 ^{b, c}	
WO ₃ -K				16.4 ^b	84.6 ^b	84.6 ^b	
Pt/WO ₃ -Y				40.6 ^a	58.8 ^a	58.8 ^a	
Pt/WO ₃ -S				32.4 ^a	48.7 ^a	48.7 ^a	
Pt/TiO ₂ -P25				{ 38.0 ^a 59.1 ^b	{ 25.9 ^a 21.8 ^b	{ 25.9 ^a 21.8 ^b	
TiO ₂ -P25				{ 13.3 ^{a, d} 33.8 ^{b, d}	{ 60.8 ^{a, d} 34 ^{b, d}	{ 60.8 ^{a, d} 34 ^{b, d}	
Pt/TiO ₂ -M				85.2 ^b	20.6 ^b	20.6 ^b	
Pt/TiO ₂ -J.				43 ^a	31 ^a	31 ^a	
				{ 48.5 ^a 11.5 ^{d, e} 38.6 ^{a, d}	{ 26.5 ^a 63 ^{d, e} 35.4 ^{a, d}	{ 26.5 ^a 63 ^{d, e} 35.4 ^{a, d}	
Fe ³⁺ impregnated TiO ₂	1–2	125 W Hg lamp UV light	Photocatalyst: 50 mg aqueous benzene (1 to 20 mM): 5 mL	-	9–15	80–86	[87]

Table 3. *Cont.*

Photocatalyst	t * (h)	Light Source	Operating Conditions	Benzene Conversion (%) X	Phenol Yield (%) η	Selectivity to Phenol (%) S _p	Ref.
Fe-Cr-TiO ₂	12	450 W mercury lamp λ = 200–400 nm	Photocatalyst: 30 mg CH ₃ CN: 2 mL benzene: 1 mL (25 wt%) H ₂ O ₂ : 2 mL	28 ± 0.5	25.2 ± 0.5	90 ± 0.5	[86]
Fe-V-Cu supported on TiO ₂	4	black light blue fluorescent bulb (8W)	Photocatalyst: 0.2 g benzene: 11 cm ³ benzene/H ₂ O ₂ mole ratio: 0.5 (30 wt%) H ₂ O ₂ : 30 cm ³ solvent: 40 cm ³ acetone ^a , acetonitrile ^b , pyridine ^c ascorbic acid: 0.5	18.61 ^a 14.27 ^b 7.9 ^c	9.68 ^a 9.7 ^b 7.11 ^c	52 ^a 68 ^b 90 ^c	[92]
LT-550			Photocatalyst: 5 mg	38.7	36.3	94	
LT-750			Benzene: 100 μ L	47.1	45.2	96	
Cu(OH) ₂ /LT-550			CH ₃ CN: 500 μ L	42	40.7	97	
Cu(OH) ₂ /LT-750	6	UV light	H ₂ O: 13 mL	49.9	48.4	97	[93]
Cu(OH) ₂ /LT-750 ^a			(30 wt%) H ₂ O ₂ : 87 μ L	^a 55.0	^a 47.9	^a 87	
Cu(OH) ₂ /LT-750 ^b				^b 41	^b 36.5	^b 89	
CuPd/g-C ₃ N ₄	1.5	solar simulator	Solution A: -photocatalyst: 20 mg - deionized water: 30 mL Solution B: - benzene: 0.5 mL - acetonitrile: 30 mL. (30 wt%) H ₂ O ₂ : 5 mmol added to the two mixed solutions.	98.1	87.8	89.6	[94]
Fe ₂ O ₃ /g-C ₃ N ₄	12			15			
Pd/g-C ₃ N ₄	12			43			
Cu/g-C ₃ N ₄	12			39			
Ni/g-C ₃ N ₄	12			20			
Ag/g-C ₃ N ₄	12			32			
FePd/g-C ₃ N ₄	12		Photocatalyst:	70			
FeCu/g-C ₃ N ₄	12		100 mg	67			
FeAg/g-C ₃ N ₄	12		Benzene:1 mmol	41			
FeNi/g-C ₃ N ₄	12	Visible light	CH ₃ CN: 5.0 mL (30 wt%) H ₂ O ₂ :	29			
PdCu/g-C ₃ N ₄	12	20 W	1.1 mmol	81			
PdNi/g-C ₃ N ₄	12		^a 50 mg of catalyst	72	–	–	[95]
PdAg/g-C ₃ N ₄	12	domestic bulb	^b 25 mg of catalyst	77			
CuNi/g-C ₃ N ₄	12		^c 15 mg of catalyst	57			
CuAg/g-C ₃ N ₄	0.5		^d methanol as a solvent	99			
CuAg/g-C ₃ N ₄ ^a	0.5		^e water as a solvent	99 ^a			
CuAg/g-C ₃ N ₄ ^b	0.5		^f ethanol as a solvent	99 ^b			
CuAg/g-C ₃ N ₄ ^c	3			99 ^c			
CuAg/g-C ₃ N ₄ ^d	0.5			86 ^d			
CuAg/g-C ₃ N ₄ ^e	0.5			83 ^e			
CuAg/g-C ₃ N ₄ ^f	0.5			99 ^f			
mpg-C ₃ N ₄				2		95	
3%FeCl ₃ /mpg-C ₃ N ₄			Photocatalyst: 25 mg	17		98	
5%FeCl ₃ /mpg-C ₃ N ₄			benzene: 4.5 mmol	38		97	
10%FeCl ₃ /mpg-C ₃ N ₄			(30 wt%) H ₂ O ₂ : 0.255 mL	23		94	
20%FeCl ₃ /mpg-C ₃ N ₄			60 °C	25		80	
5%FeCl ₃ /mpg-C ₃ N ₄ ^a	4	100 W mercury lamp	^a T = 25 °C	4 ^a	–	99 ^a	[75]
5%FeCl ₃ /mpg-C ₃ N ₄ ^b			^b T = 40 °C	10 ^b		96 ^b	
5%FeCl ₃ /mpg-C ₃ N ₄ ^c		λ > 420nm	^c T = 80 °C	21 ^c		81 ^c	
5%FeCl ₃ /mpg-C ₃ N ₄ ^d			^d H ₂ O ₂ : 0.510 mL	44 ^d		85 ^d	
5%FeCl ₃ /mpg-C ₃ N ₄ ^e			^e H ₂ O ₂ : 0.765 mL	47 ^e		60 ^e	
g-C ₃ N ₄					0		
mpg-C ₃ N ₄					2.0		
FeCl ₃					0.5		
5%Fe-g-C ₃ N ₄			Photocatalyst:		1.8		
10%Fe-g-C ₃ N ₄			50 mg		4.8		
20%Fe-g-C ₃ N ₄			CH ₃ CN: 4 mL		2.5		
20%Fe-g-C ₃ N ₄ /Cu-g	4	500 W Xenon lamp	benzene: 0.8 mL	–	1.4	–	[73]
Ti-g-C ₃ N ₄			H ₂ O: 4 mL		0.1		
Ni-g-C ₃ N ₄		λ > 420 nm	(30 wt%)H ₂ O ₂ :		0.1		
Zn-g-C ₃ N ₄			0.51 mL		0.1		
Fe/SBA-15					1.0		
g-C ₃ N ₄ /SBA-15					0.1		
Fe-g-C ₃ N ₄ /SBA-15					11.9		

Table 3. Cont.

Photocatalyst	t * (h)	Light Source	Operating Conditions	Benzene Conversion (%) X	Phenol Yield (%) η	Selectivity to Phenol (%) S_p	Ref.
10%Fe-g-C ₃ N ₄ 20%Fe-g-C ₃ N ₄ 30%Fe-g-C ₃ N ₄ 10%Fe-g-C ₃ N ₄ -LUS-1 20%Fe-g-C ₃ N ₄ -LUS-1	4	sunlight	Photocatalyst: 0.05 g benzene: 1 mL CH ₃ CN: 4 mL H ₂ O ₂ : 0.5 mL T = 60 °C	–	6.5 8 10.5 10 16	>90 ~90 ~90 >90 >90	[96]
Fe-CN TS-1 Fe-CN/TS-1-1 ^a Fe-CN/TS-1-2 ^b Fe-CN/TS-1-3 ^c Fe-CN/TS-1-4 ^d Fe-CN/TS-1-5 ^e Fe-CN/TS-1-6 ^f Fe-CN/TS-1-7 ^g Fe-CN/TS-1-8 ^h Fe-CN/TS-1-9 ⁱ Fe/TS-1	4	300 W Xenon lamp $\lambda > 420$ nm	CH ₃ CN: 4 mL benzene: 0.8 mL H ₂ O: 4 mL (30 wt%) H ₂ O ₂ : 0.51 mL 60 °C pH = 7 Fe-CN/TS-1-X ^a X = 1 for 10% dicyandiamide/TS-1 ^b X = 2 for 20% dicyandiamide/TS-1 ^c X = 3 for 50% dicyandiamide/TS-1 ^d X = 4 for 100% dicyandiamide/TS-1 ^e X = 5 for 200% dicyandiamide/TS-1 Fe-CN/TS-1-X ^f X = 6 for 5% FeCl ₃ /dicyandiamide ^g X = 2 for 10% FeCl ₃ /dicyandiamide ^h X = 7 for 20% FeCl ₃ /dicyandiamide ⁱ X = 8 for 50% FeCl ₃ /dicyandiamide	–	1.1 2.4 2.8 ^a 10 ^b 8.8 ^c 1.3 ^d 0.1 ^e 1.4 ^f 10 ^g 5 ^h 1.6 ⁱ 7.6	–	[97]
MIL-100(Fe) MIL-68(Fe) ⁱ	8	Visible light irradiation $\lambda \geq 420$ nm	Photocatalyst: 10 mg H ₂ O ₂ : 0.5 mmol Solvent: 4 mL ^a CH ₃ CN solvent H ₂ O ₂ :benzene(1:2) ^b Acetone solvent H ₂ O ₂ :benzene(1:2) ^c H ₂ O solvent H ₂ O ₂ :benzene(1:2) ^d DMF solvent H ₂ O ₂ :benzene(1:2) ^e CH ₃ CN:H ₂ O (1:1) H ₂ O ₂ :benzene(1:2) ^f CH ₃ CN:H ₂ O (1:1) H ₂ O ₂ :benzene(3:4) ^g CH ₃ CN:H ₂ O (1:1) H ₂ O ₂ :benzene(2:2) ^h CH ₃ CN:H ₂ O (1:1) H ₂ O ₂ :benzene(3:2) ⁱ CH ₃ CN:H ₂ O (1:1) H ₂ O ₂ :benzene(3:4)	10.3 ^a 2.4 ^b 8.3 ^c 3.3 ^d 13.6 ^e 20.1 ^f 21.7 ^g 22.5 ^h 14 ⁱ	10.3 ^a 2.38 ^b 7.1 ^c 2.5 ^d 13.3 ^e 14.77 ^f 20.8 ^g 31.05 ^h 9.45 ⁱ	>99 ^a 99 ^b 85 ^c 76 ^d 98 ^e 98 ^f 96 ^g 92 ^h 90 ⁱ	[98]
Ti/CNT Cu/Ti/CNT	0.75	Low-pressur mercury lamp	Photocatalyst: 100 mg benzene: 20 mL H ₂ O: 20 mL	53.8 68.3	35.1 51.8	65.3 75.8	[99]
Zn-Ti-LDH	3	300 W Xenon lamp	Photocatalyst: 20 mg Benzene: 0.2 mmol H ₂ O: 20 mL	5.65	4.59	87.18	[100]
Bi ₂ WO ₆ /CdWO ₄ composite	3	300 W Xe lamp $\lambda \geq 400$ nm	Photocatalyst: 50 mg benzene: 0.5 mmol CH ₃ CN: 3 mL H ₂ O: 100 μ L O ₂ : 3 mL min ⁻¹	5.8	–	>99	[72]
QuCN ⁺ ion	1	500 W xenon lamp $\lambda =$ 290–600 nm	[QuCN ⁺]: 2.0 mM [C ₆ H ₆]: 30 mM [H ₂ O]: 3.0 M	31	30	98	[76]

* t = irradiation time, min.

Shiraishi et al. considered TiO₂ with a mesoporous structure (mTiO₂) synthesized through the surfactant-templating method and aggregation method consisting of the nanosized TiO₂ (nTiO₂) particle combination followed by sintering of the particles [88].

In particular, they underlined that the presence of “mesopores” allows a smooth diffusion of molecules, which is indispensable for the adsorption-driven activity. As can be seen from Table 3, the use of the TiO₂ sample with a mesoporous structure showed a higher yield and selectivity to phenol (>80%) than TiO₂ with a nonporous structure [88].

Yuzawa et al. studied the direct hydroxylation of benzene in water using a Pt/TiO₂ photocatalyst [89]. In this photocatalytic reaction system, the selection of the wavelength associated with the incident light wavelength, exclusion of oxygen, and optimization of platinum loading amount were important factors to achieve selective phenol production. When Pt/TiO₂ was irradiated, the formation of phenol and small amounts of biphenyl, cyclohexanol, cyclohexanone, and carbon dioxide were detected according to the following steps (Figure 6):

- (1) hydroxylation of benzene with water;
- (2) coupling of benzene;
- (3) reduction of the produced phenol and successive oxidation of the produced cyclohexanol to cyclohexanone;
- (4) decomposition of benzene with water.

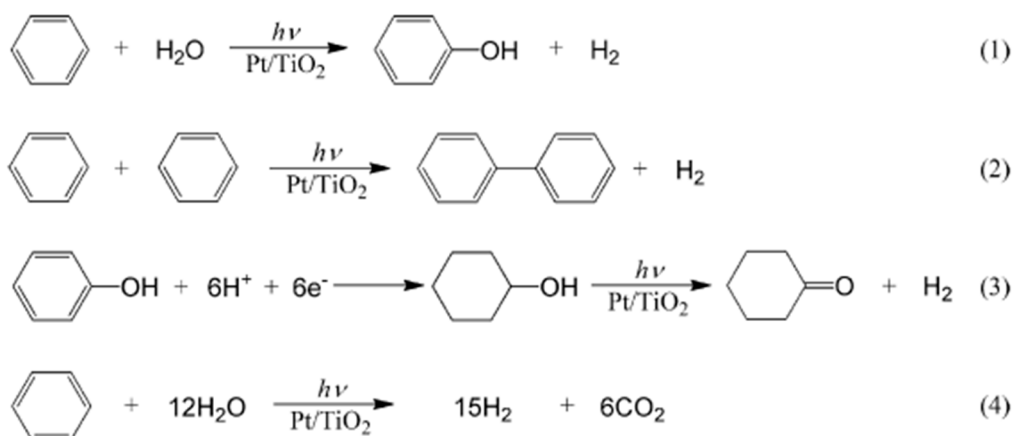


Figure 6. Chemical reactions involving aromatic ring species under light irradiation using Pt/TiO₂. Reprinted with permission from [89]. Copyright (2012) American Chemical Society.

Despite the fact that the phenol selectivity was high (88%), an excess amount of hydrogen (95 μmol) was also produced. However, when the irradiation wavelength was longer than 385 nm, higher phenol selectivity (91%) was obtained with no production of biphenyl, carbon dioxide, and hydrogen. Thus, the irradiation wavelength appears as a factor to be considered for obtaining the selective aromatic ring hydroxylation of benzene.

Moreover, it was shown that the presence of air or oxygen effectively promotes complete benzene oxidation to carbon dioxide and water [101], according to the reaction reported in Figure 7:

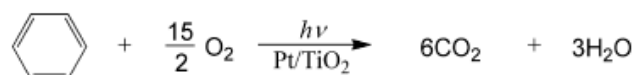


Figure 7. Oxidation reaction of benzene to carbon dioxide and water under light irradiation. Reprinted with permission from [89]. Copyright (2012) American Chemical Society.

Thus, the absence of oxygen in the reactor is required to achieve high selectivity to phenol. The relationship between the platinum loading amount and the product yield was also identified.

The sample with 0.1 wt% of platinum loaded onto the TiO₂ surface exhibited the highest phenol yield. Thus, the optimum Pt amount for phenol production was found to be 0.1 wt% because phenol selectivity equal to 91% was obtained.

Yusuke et al. reported a versatile way to modify the efficiency and phenol selectivity of heterogeneous photocatalytic oxidation [90]. They found that the sunlight-induced photocatalytic oxidation activity of aqueous benzene to phenol on Au/TiO₂ nanoparticles was improved when the reaction was carried out under CO₂ atmosphere (230 kPa). In more detail, benzene is directly oxidized to phenol and the produced phenol is further converted to more oxidized products, such as catechol, hydroxyquinone, and trihydroxybenzenes, and finally mineralized to CO₂. On the contrary, when the reaction is carried out under CO₂ pressure, the presence of carbon dioxide probably suppressed the successive oxidation of phenol, increasing the yield and selectivity to phenol [90].

Devaraji et al. studied the photoactivity of TiO₂, V-doped TiO₂, and Au-V-doped TiO₂ under UV irradiation. V-doped TiO₂ showed benzene conversion equal to 3% with 100% phenol selectivity after 6 h of irradiation time [102]. The same authors evidenced that the level of benzene conversion increased linearly from 3% to 13% by increasing the irradiation time from 6 to 24 h, respectively. After Au deposition, the photocatalytic activity strongly increased because the incorporation of V in the TiO₂ lattice generated a V⁵⁺ energy level below the conduction band of TiO₂, which helped to trap the excited electrons, whereas Au deposited over V-doped TiO₂ acted as an electron sink [102].

As an alternative to TiO₂ as support for noble metals, WO₃ has been considered. In particular, Pt/WO₃ photocatalysts showed much higher selectivity to phenol than commercial TiO₂ and Pt/TiO₂ [91]. In particular, the photocatalytic reaction using Pt/WO₃-K (Table 3) showed the highest selective phenol production, with ~74% of selectivity and with ~69% of benzene conversion after 240 min of UV irradiation time. The production of phenol was also observed with the Pt/TiO₂ photocatalyst but the phenol production was saturated within 60 min of UV irradiation, with a noticeable increase in the CO₂ gaseous phase, indicating that there was further oxidation of the generated phenol. Instead, after 60 min of visible light irradiation ($\lambda > 400$ nm), better phenol selectivity (~84%) was reported with Pt/WO₃-K (Table 3).

In the same paper, considering an aqueous benzene solution, it has been reported that hydroxyl radicals ($\bullet$ OH) are produced through the reaction of photogenerated holes with water molecules adsorbed on the photocatalyst surface. The hydroxyl radical reacts with benzene to generate hydroxylated benzene radical, which is then oxidized by a positive hole on the photocatalyst surface and deprotonated, producing phenol (Figure 8).

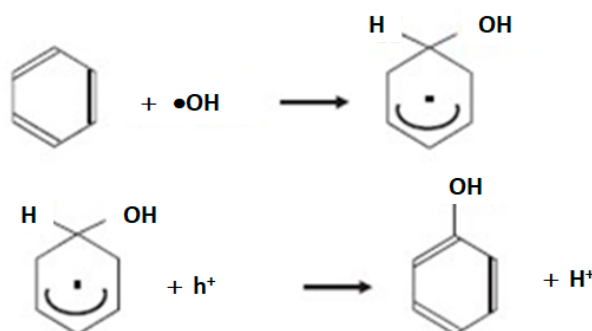


Figure 8. Formation of the hydroxylated benzene radical and next deprotonation with phenol generation [91].

Considering the previous papers, it appears that noble metals deposited on the TiO₂ surface act as a good co-catalyst to improve the photoactivity. At the same time, these elements are quite expensive and, therefore, many efforts have devoted to replacing them with low-cost materials [91]. This led to the design of new, low-cost, and efficient photocatalysts that yield high benzene conversion and high selectivity to phenol at ambient temperature and pressure. The surface properties of TiO₂

have been modified by metal impregnation in order to increase the phenol production as well as its selectivity. In this regard, Gupta et al. reported the oxidation of benzene to phenol under UV irradiation using Fe^{3+} (at 5 wt%) impregnated on a TiO_2 catalyst [87]. The experimental tests revealed that the optimum selectivity to phenol (80–86%) was achieved during 1–2 h of UV irradiation time. The enhanced photoactivity of the Fe^{3+} impregnated on TiO_2 is probably caused by the structural defects induced by the presence of Fe^{3+} ions on the TiO_2 surface [103].

Some interest is also directed towards doping TiO_2 with metallic elements to broaden the absorption spectrum into the visible range. In particular, the TiO_2 doping with transition metal ions like Cr, Fe, and V leads to the generation of a new acceptor level in the conduction band of TiO_2 , which acts as an electron trapping center, increasing the number of holes available in the valence band, and simultaneously promotes the reduction of molecular oxygen to H_2O_2 during the photocatalytic reaction. The doping of TiO_2 with Fe enhances the photocatalytic activity because it allows an increase in the electron transfer process and the electron-hole separation, thus minimizing charge carrier recombination. This minimization of charge carrier recombination is essential for redox reactions [104].

Experimental tests on the photocatalytic oxidation reaction of benzene to phenol under UV or visible light irradiation were conducted by Perumal et al. [86] using Fe–Cr-doped TiO_2 . It was shown that, after 12 h of UV irradiation time, 28% of benzene conversion and 90% selectivity to phenol were achieved with H_2O_2 as oxidant (Table 3). These results evidenced that the simultaneous presence of Cr and Fe in the TiO_2 lattice led to higher photocatalytic activity towards phenol production if compared with Fe-doped TiO_2 and Cr-doped TiO_2 . Additionally, Fe–Cr-doped TiO_2 also showed visible light absorption but low benzene conversion was observed even after 24 h of visible light irradiation, suggesting that the photocatalytic activity for benzene oxidation depends on the valence band position of TiO_2 and that, under visible light irradiation, a small number of holes were produced as compared to those generated upon UV light irradiation [105]. Figure 9 shows the possible reaction mechanism on Fe–Cr-doped TiO_2 in which phenol is produced via two reaction paths (path-A and path-B).

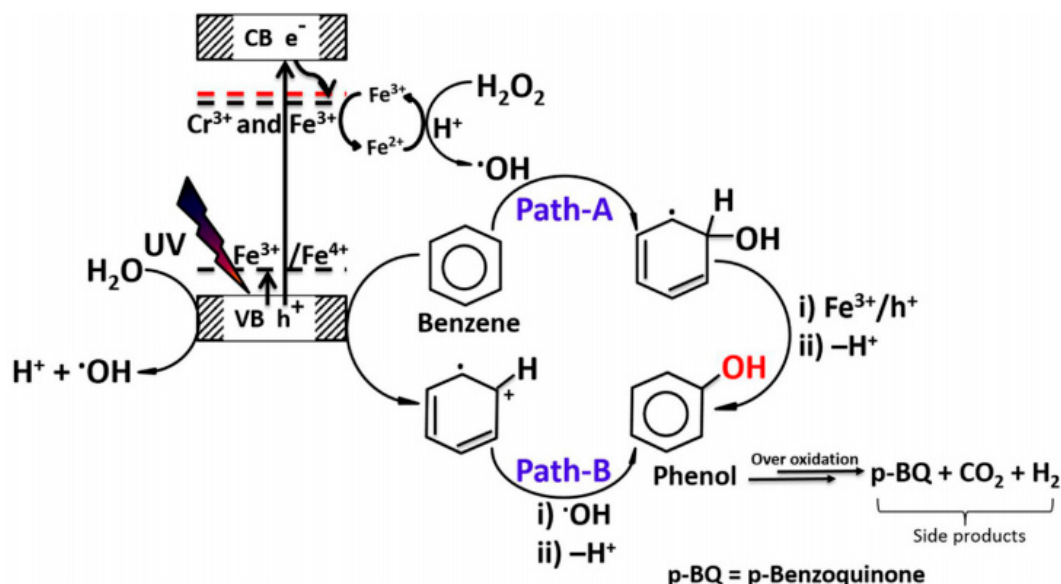


Figure 9. Possible mechanism of photocatalytic benzene oxidation to phenol using Fe–Cr-doped TiO_2 . Reprinted from [86], Copyright (2018), with permission from Elsevier.

In the presence of UV light, electrons are promoted from the valence band (VB) to the conduction band (CB). In path-A, the trapped electrons in the dopant level can reduce Fe^{3+} to Fe^{2+} , which then is able to react with H_2O_2 and a proton (coming from H_2O) to produce a hydroxyl radical and Fe^{3+} . The hydroxyl radical originates from both water and H_2O_2 and they attack the aromatic benzene ring to form hydroxycyclohexadienyl radicals [106]. The photogenerated positive holes in the VB or

Fe^{3+} oxidize the hydroxycyclohexadienyl radicals to phenol via a deprotonation process to restart the photocatalytic cyclic reaction [107]. In path-B, the generated holes in the VB react with benzene to produce benzene radical ions. These radical ions react with hydroxyl radicals, forming phenol, probably via deprotonation of an unstable intermediate.

To obtain higher selectivity to phenol as well as better conversion of benzene, the researchers focused their attention on more complex systems (composite photocatalysts) that showed excellent photocatalytic performance. In this regard, carbon nitride materials were extensively considered (Table 3). For example, Zhang and Park studied CuPd bimetallic alloy nanoparticle-coated holey carbon nitride materials ($\text{g-C}_3\text{N}_4/\text{CuPd}$) as photocatalyst [94]. Compared with bare $\text{g-C}_3\text{N}_4$, a significant increase in phenol selectivity is achieved when CuPd bimetallic alloy nanoparticles are uniformly dispersed on the support surface. The catalyst containing 0.5 wt% of CuPd bimetallic alloy particles showed high photocatalytic activity in the oxidation of benzene to phenol (benzene conversion: 98.1% and selectivity to phenol: 89.6%) after 90 min of solar irradiation, probably linked to the uniform distribution of CuPd bimetallic alloy nanoparticles and the synergistic effect between CuPd particles and $\text{g-C}_3\text{N}_4$. These two factors may contribute to the improvement of both solar energy use and the photo-induced electron-hole pairs, resulting in enhanced performance for the selective benzene oxidation to phenol [94].

Zhang et al. also focused their attention on the synthesis of phenol under visible light irradiation using a physical mixture of Fe salts (FeCl_3 or FeCl_2) and mesoporous carbon nitride ($\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$). The reactions were carried out with water–acetonitrile as solvents and H_2O_2 as oxidant using $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ samples with different FeCl_3 loadings (in the range 3–20 wt%). The 5 wt% $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$ photocatalyst evidenced a benzene conversion of ~38% and a phenol selectivity equal to 97%. They also investigated the possible mechanism under visible light (Figure 10). In detail, two main steps are involved in the visible light oxidation of benzene to phenol: the electrons generated by light irradiation reduce Fe^{3+} to Fe^{2+} , which is able to decompose H_2O_2 with the formation of $\cdot\text{OH}$. The hydroxylation of benzene by $\cdot\text{OH}$ produces a cyclohexadienyl radical intermediate (A) and then the positive hole (h^+) of $\text{mpg-C}_3\text{N}_4$ oxidizes A to phenol.

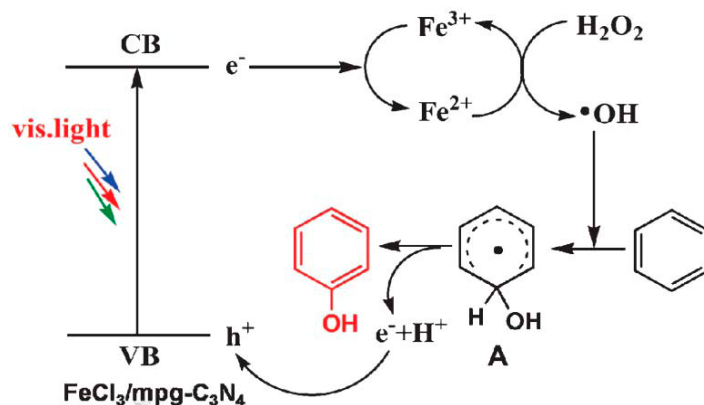


Figure 10. Possible reaction mechanism for the catalytic oxidation of benzene by $\text{FeCl}_3/\text{mpg-C}_3\text{N}_4$. Reproduced from [75] with permission from The Royal Society of Chemistry.

In some cases, metal–organic framework (MOF)-based photocatalysts also evidenced significant photoactivity under visible light. For example, Wang et al. [98] studied selective benzene hydroxylation to phenol over two Fe-based MOFs (MIL-100(Fe) and MIL-68(Fe)) under visible light irradiation using H_2O_2 as oxidant. MIL-100(Fe) showed much intensive absorption in the visible light region compared with MIL-68(Fe), which could justify its enhanced photocatalytic performance. In fact, the MIL-100(Fe) photocatalyst evidenced a benzene conversion equal to 20.1% and higher selectivity to phenol (98%). Instead, lower benzene conversion (14%) and selectivity to phenol (90%) were observed over MIL-68(Fe).

Another studied material was a Zn₂Ti-layered double hydroxide (ZnTi-LDH) photocatalyst, which showed an enhancement of photoinduced charge carrier separation due to the presence of oxygen vacancies on the LDH surface and an increase in superoxide radicals [100]. The band structure of the ZnTi-LDH photocatalyst allowed the realization of advanced activity, with selectivity to phenol equal to 87.18% in water with air as oxidant under UV-vis light irradiation.

4. Concluding Remarks and Perspectives

The one-step oxidation of benzene to phenol in the liquid phase has been extensively studied from a scientific point of view in recent years due to the importance of phenol in industrial chemistry. Several catalysts and photocatalysts (both homogenous and heterogeneous) able to work under mild conditions were proposed in the literature and special attention to the reaction mechanism was also given in most papers. Despite some catalytic formulations showing significant benzene conversion and phenol selectivity, it must be taken into account that one of the main difficulties in performing the selective oxidation of benzene is that the desired product (phenol) is easily over-oxidized to hydroxyphenols and finally oxidized into carbon dioxide. Therefore, it is still essential to study deeply and/or to develop new catalytic and photocatalytic materials able to achieve high selectivity to phenol at high conversion of benzene and, as a consequence, to ensure high phenol yield. One promising strategy could be the formulation of supports for active phases (photocatalytic or not) with high benzene adsorption capacity and with low affinity towards phenol in a manner to prevent further oxidation reactions of the desired product.

Additionally, most catalytic formulations were studied in slurry reactors. Therefore, in response to the question asked in the title of this review article, there is still a need to consider three main aspects for the possible industrialization of a catalytic reactor devoted to the one-step oxidation of benzene to phenol in the liquid phase:

- the immobilization of the catalysts or photocatalysts on macroscopic supports (i.e., the development of structured catalysts) to avoid the separation of catalyst powders from the liquid phase containing phenol at the end of the oxidation step;
- the development of structured catalysts or photocatalysts with high stability and which are easily recyclable;
- the development of novel selective oxidation systems (e.g., highly efficient photoanodes for the photoelectrocatalytic oxidation of benzene to phenol);
- the design of efficient and low-cost systems to recover the produced phenol from the liquid phase.

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References

1. Schmidt, R.J. Industrial catalytic processes—Phenol production. *Appl. Catal. A Gen.* **2005**, *280*, 89–103. [\[CrossRef\]](#)
2. Solyman, W.S.; Nagiub, H.M.; Alian, N.A.; Shaker, N.O.; Kandil, U.F. Synthesis and characterization of phenol/formaldehyde nanocomposites: Studying the effect of incorporating reactive rubber nanoparticles or Cloisite-30B nanoclay on the mechanical properties, morphology and thermal stability. *J. Radiat. Res. Appl. Sci.* **2017**, *10*, 72–79. [\[CrossRef\]](#)
3. Pryde, C.; Hellman, M. Solid state hydrolysis of bisphenol-A polycarbonate. I. Effect of phenolic end groups. *J. Appl. Polym. Sci.* **1980**, *25*, 2573–2587. [\[CrossRef\]](#)
4. Takeichi, T.; Furukawa, N. Epoxy Resins and Phenol-Formaldehyde Resins. In *Polymer Science: A Comprehensive Reference*; Elsevier BV: Amsterdam, The Netherlands, 2012; pp. 723–751.

5. Brydson, J.A. *Plastics Materials*; Elsevier: Amsterdam, The Netherlands, 1999.
6. Zakoshansky, V. The cumene process for phenol-acetone production. *Pet. Chem.* **2007**, *47*, 273–284. [CrossRef]
7. Fortuin, J.; Waterman, H. Production of phenol from cumene. *Chem. Eng. Sci.* **1953**, *2*, 182–192. [CrossRef]
8. The Essential Chemical Industry—Online. Available online: <https://www.essentialchemicalindustry.org/chemicals/phenol.html> (accessed on 2 October 2020).
9. Park, H.; Choi, W. Photocatalytic conversion of benzene to phenol using modified TiO₂ and polyoxometalates. *Catal. Today* **2005**, *101*, 291–297. [CrossRef]
10. Molinari, R.; Poerio, T. Remarks on studies for direct production of phenol in conventional and membrane reactors. *Asia Pac. J. Chem. Eng.* **2010**, *5*, 191–206. [CrossRef]
11. Fukuzumi, S.; Ohkubo, K. One-Step Selective Hydroxylation of Benzene to Phenol. *Asian J. Org. Chem.* **2015**, *4*, 836–845. [CrossRef]
12. Ottenbacher, R.V.; Talsi, E.P.; Bryliakov, K.P. Recent progress in catalytic oxygenation of aromatic C–H groups with the environmentally benign oxidants H₂O₂ and O₂. *Appl. Organomet. Chem.* **2020**, *34*, e5900. [CrossRef]
13. Jiang, T.; Wang, W.; Han, B. Catalytic hydroxylation of benzene to phenol with hydrogen peroxide using catalysts based on molecular sieves. *New J. Chem.* **2013**, *37*, 1654–1664. [CrossRef]
14. Wanna, W.H.; Janmanchi, D.; Thiyagarajan, N.; Ramu, R.; Tsai, Y.-F.; Yu, S.S. Selective Oxidation of Simple Aromatics Catalyzed by Nano-Biomimetic Metal Oxide Catalysts: A Mini Review. *Front. Chem.* **2020**, *8*, 589178. [CrossRef] [PubMed]
15. Yuranov, I.; Bulushev, D.A.; Renken, A.; Kiwi-Minsker, L. Benzene to phenol hydroxylation with N₂O over Fe-Beta and Fe-ZSM-5: Comparison of activity per Fe-site. *Appl. Catal. A Gen.* **2007**, *319*, 128–136. [CrossRef]
16. Guo, H.; Chen, Z.; Mei, F.; Zhu, D.; Xiong, H.; Yin, G. Redox Inactive Metal Ion Promoted C–H Activation of Benzene to Phenol with PdII (bpym): Demonstrating New Strategies in Catalyst Designs. *Chem. Asian J.* **2013**, *8*, 888–891. [CrossRef] [PubMed]
17. Hu, L.; Wang, C.; Ye, L.; Wu, Y.; Yue, B.; Chen, X.; He, H. Direct hydroxylation of benzene to phenol using H₂O₂ as an oxidant over vanadium-containing mesoporous carbon catalysts. *Appl. Catal. A Gen.* **2015**, *504*, 440–447. [CrossRef]
18. Parida, K.; Rath, D. Structural properties and catalytic oxidation of benzene to phenol over CuO-impregnated mesoporous silica. *Appl. Catal. A Gen.* **2007**, *321*, 101–108. [CrossRef]
19. Niwa, S.-i.; Eswaramoorthy, M.; Nair, J.; Raj, A.; Itoh, N.; Shoji, H.; Namba, T.; Mizukami, F. A one-step conversion of benzene to phenol with a palladium membrane. *Science* **2002**, *295*, 105–107. [CrossRef]
20. Al-Sabagh, A.; Yehia, F.; Eshaq, G.; ElMetwally, A. Eclectic hydroxylation of benzene to phenol using ferrites of Fe and Zn as durable and magnetically retrievable catalysts. *ACS Sustain. Chem. Eng.* **2017**, *5*, 4811–4819. [CrossRef]
21. Monfared, H.H.; Amouei, Z. Hydrogen peroxide oxidation of aromatic hydrocarbons by immobilized iron (III). *J. Mol. Catal. A Chem.* **2004**, *217*, 161–164. [CrossRef]
22. Lyu, Y.-J.; Qi, T.; Yang, H.-Q.; Hu, C.-W. Performance of edges on carbon for the catalytic hydroxylation of benzene to phenol. *Catal. Sci. Technol.* **2018**, *8*, 176–186. [CrossRef]
23. Yamada, M.; Karlin, K.D.; Fukuzumi, S. One-step selective hydroxylation of benzene to phenol with hydrogen peroxide catalysed by copper complexes incorporated into mesoporous silica–alumina. *Chem. Sci.* **2016**, *7*, 2856–2863. [CrossRef]
24. Wanna, W.H.; Ramu, R.; Janmanchi, D.; Tsai, Y.-F.; Thiyagarajan, N.; Yu, S.S.-F. An efficient and recyclable copper nano-catalyst for the selective oxidation of benzene to p-benzoquinone (p-BQ) using H₂O₂ (aq) in CH₃CN. *J. Catal.* **2019**, *370*, 332–346. [CrossRef]
25. Peng, J.; Shi, F.; Gu, Y.; Deng, Y. Highly selective and green aqueous–ionic liquid biphasic hydroxylation of benzene to phenol with hydrogen peroxide. *Green Chem.* **2003**, *5*, 224–226. [CrossRef]
26. Nomiya, K.; Yagishita, K.; Nemoto, Y.; Kamataki, T.-a. Functional action of Keggin-type mono-vanadium (V)-substituted heteropolymolybdate as a single species on catalytic hydroxylation of benzene in the presence of hydrogen peroxide. *J. Mol. Catal. A Chem.* **1997**, *126*, 43–53. [CrossRef]
27. Jiang, W.; Zhu, W.; Li, H.; Chao, Y.; Xun, S.; Chang, Y.; Liu, H.; Zhao, Z. Mechanism and optimization for oxidative desulfurization of fuels catalyzed by Fenton-like catalysts in hydrophobic ionic liquid. *J. Mol. Catal. A Chem.* **2014**, *382*, 8–14. [CrossRef]
28. Anandababu, K.; Muthuramalingam, S.; Velusamy, M.; Mayilmurugan, R. Single-step benzene hydroxylation by cobalt (ii) catalysts via a cobalt (iii)-hydroperoxo intermediate. *Catal. Sci. Technol.* **2020**, *10*, 2540–2548. [CrossRef]

29. Muthuramalingam, S.; Anandababu, K.; Velusamy, M.; Mayilmurugan, R. One step phenol synthesis from benzene catalysed by nickel (ii) complexes. *Catal. Sci. Technol.* **2019**, *9*, 5991–6001. [\[CrossRef\]](#)
30. You, X.; Wei, Z.; Wang, H.; Li, D.; Liu, J.; Xu, B.; Liu, X. Synthesis of two copper clusters and their catalysis towards the oxidation of benzene into phenol. *RSC Adv.* **2014**, *4*, 61790–61798. [\[CrossRef\]](#)
31. Kulakova, A.N.; Bilyachenko, A.N.; Levitsky, M.M.; Khrustalev, V.N.; Korlyukov, A.A.; Zubavichus, Y.V.; Dorovatovskii, P.V.; Lamaty, F.; Bantreil, X.; Villemejeanne, B. Si₁₀Cu₆N₄ cage hexacoppersilsesquioxanes containing N ligands: Synthesis, structure, and high catalytic activity in peroxide oxidations. *Inorg. Chem.* **2017**, *56*, 15026–15040. [\[CrossRef\]](#)
32. Tsuji, T.; Zaoputra, A.A.; Hitomi, Y.; Mieda, K.; Ogura, T.; Shiota, Y.; Yoshizawa, K.; Sato, H.; Kodera, M. Specific enhancement of catalytic activity by a dicopper core: Selective hydroxylation of benzene to phenol with hydrogen peroxide. *Angew. Chem. Int. Ed.* **2017**, *129*, 7887–7890. [\[CrossRef\]](#)
33. Conde, A.; Diaz-Requejo, M.M.; Pérez, P.J. Direct, copper-catalyzed oxidation of aromatic C–H bonds with hydrogen peroxide under acid-free conditions. *Chem. Commun.* **2011**, *47*, 8154–8156. [\[CrossRef\]](#)
34. Kumari, S.; Muthuramalingam, S.; Dhara, A.K.; Singh, U.; Mayilmurugan, R.; Ghosh, K. Cu (I) complexes obtained via spontaneous reduction of Cu (II) complexes supported by designed bidentate ligands: Bioinspired Cu (I) based catalysts for aromatic hydroxylation. *Dalton Trans.* **2020**, *49*, 13829–13839. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Kudrik, E.V.; Sorokin, A.B. N-Bridged Diiron Phthalocyanine Catalyzes Oxidation of Benzene with H₂O₂ via Benzene Oxide with NIH Shift Evidenced by Using 1, 3, 5-[D₃] Benzene as a Probe. *Chem. Eur. J.* **2008**, *14*, 7123–7126. [\[PubMed\]](#)
36. Raba, A.; Cokoja, M.; Herrmann, W.A.; Kühn, F.E. Catalytic hydroxylation of benzene and toluene by an iron complex bearing a chelating di-pyridyl-di-NHC ligand. *Chem. Commun.* **2014**, *50*, 11454–11457. [\[CrossRef\]](#) [\[PubMed\]](#)
37. Ramu, R.; Wanna, W.H.; Janmanchi, D.; Tsai, Y.-F.; Liu, C.-C.; Mou, C.-Y.; Yu, S.S.-F. Mechanistic study for the selective oxidation of benzene and toluene catalyzed by Fe (ClO₄)₂ in an H₂O₂–H₂O–CH₃CN system. *Mol. Catal.* **2017**, *441*, 114–121. [\[CrossRef\]](#)
38. Yalymov, A.I.; Bilyachenko, A.N.; Levitsky, M.M.; Korlyukov, A.A.; Khrustalev, V.N.; Shul’pina, L.S.; Dorovatovskii, P.V.; Es’kova, M.A.; Lamaty, F.; Bantreil, X. High catalytic activity of heterometallic (Fe₆Na₇ and Fe₆Na₆) cage silsesquioxanes in oxidations with peroxides. *Catalysts* **2017**, *7*, 101. [\[CrossRef\]](#)
39. Vinogradov, M.M.; Kozlov, Y.N.; Nesterov, D.S.; Shul’pina, L.S.; Pombeiro, A.J.; Shul’pin, G.B. Oxidation of hydrocarbons with H₂O₂/O₂ catalyzed by osmium complexes containing p-cymene ligands in acetonitrile. *Catal. Sci. Technol.* **2014**, *4*, 3214–3226. [\[CrossRef\]](#)
40. Sarma, B.B.; Carmieli, R.; Collauto, A.; Efremenko, I.; Martin, J.M.; Neumann, R. Electron transfer oxidation of benzene and aerobic oxidation to phenol. *ACS Catal.* **2016**, *6*, 6403–6407. [\[CrossRef\]](#)
41. Li, X.; Xue, H.; Lin, Q.; Yu, A. Amphiphilic poly (ionic liquid)/Wells–Dawson-type phosphovanadomolybdate ionic composites as efficient and recyclable catalysts for the direct hydroxylation of benzene with H₂O₂. *Appl. Organomet. Chem.* **2020**, *34*, e5606. [\[CrossRef\]](#)
42. Carneiro, L.; Silva, A.R. Selective direct hydroxylation of benzene to phenol with hydrogen peroxide by iron and vanadyl based homogeneous and heterogeneous catalysts. *Catal. Sci. Technol.* **2016**, *6*, 8166–8176. [\[CrossRef\]](#)
43. Dong, Y.; Niu, X.; Song, W.; Wang, D.; Chen, L.; Yuan, F.; Zhu, Y. Facile synthesis of vanadium oxide/reduced graphene oxide composite catalysts for enhanced hydroxylation of benzene to phenol. *Catalysts* **2016**, *6*, 74. [\[CrossRef\]](#)
44. Shijina, A.V.; Renuka, N.K. Single step conversion of benzene to phenol using hydrogen peroxide over modified V₂O₅–Al₂O₃ systems. *React. Kinet. Catal. Lett.* **2009**, *98*, 139–147. [\[CrossRef\]](#)
45. Peng, G.; Fu, Z.; Yin, D.; Zhong, S.; Yang, Y.; Yu, N.; Yin, D. A Promising Coupled Process of Pd/γ-Al₂O₃–NH₄VO₃ Catalyzing the Hydroxylation of Benzene with Hydrogen Peroxide Produced In Situ by an Anthraquinone Redox Route. *Catal. Lett.* **2007**, *118*, 270–274. [\[CrossRef\]](#)
46. Jiang, W.-F.; Wang, W.; Wang, H.-L.; Li, Z.-Q. Photooxidation of benzene to phenol by Al₂O₃-supported Fe (III)-5-sulfosalicylic acid (ssal) complex. *Catal. Lett.* **2009**, *130*, 463–469. [\[CrossRef\]](#)
47. Miyahara, T.; Kanzaki, H.; Hamada, R.; Kuroiwa, S.; Nishiyama, S.; Tsuruya, S. Liquid-phase oxidation of benzene to phenol by CuO–Al₂O₃ catalysts prepared by co-precipitation method. *J. Mol. Catal. A Chem.* **2001**, *176*, 141–150. [\[CrossRef\]](#)

48. Masumoto, Y.-k.; Hamada, R.; Yokota, K.; Nishiyama, S.; Tsuruya, S. Liquid-phase oxidation of benzene to phenol by vanadium catalysts in aqueous solvent with high acetic acid concentration. *J. Mol. Catal. A Chem.* **2002**, *184*, 215–222. [[CrossRef](#)]
49. Miyake, T.; Hamada, M.; Sasaki, Y.; Oguri, M. Direct synthesis of phenol by hydroxylation of benzene with oxygen and hydrogen. *Appl. Catal. A Gen.* **1995**, *131*, 33–42. [[CrossRef](#)]
50. Lemke, K.; Ehrich, H.; Lohse, U.; Berndt, H.; Jähnisch, K. Selective hydroxylation of benzene to phenol over supported vanadium oxide catalysts. *Appl. Catal. A Gen.* **2003**, *243*, 41–51. [[CrossRef](#)]
51. Tanarungsun, G.; Kiatkittipong, W.; Praserttham, P.; Yamada, H.; Tagawa, T.; Assabumrungrat, S. Ternary metal oxide catalysts for selective oxidation of benzene to phenol. *J. Ind. Eng. Chem.* **2008**, *14*, 596–601. [[CrossRef](#)]
52. Tanarungsun, G.; Kiatkittipong, W.; Praserttham, P.; Yamada, H.; Tagawa, T.; Assabumrungrat, S. Hydroxylation of benzene to phenol on Fe/TiO₂ catalysts loaded with different types of second metal. *Catal. Commun.* **2008**, *9*, 1886–1890. [[CrossRef](#)]
53. Lee, C.W.; Lee, W.J.; Park, Y.K.; Park, S.-E. Catalytic hydroxylation of benzene over vanadium-containing molecular sieves. *Catal. Today* **2000**, *61*, 137–141. [[CrossRef](#)]
54. He, J.; Xu, W.-p.; Evans, D.G.; Duan, X.; Li, C.-y. Role of pore size and surface properties of Ti-MCM-41 catalysts in the hydroxylation of aromatics in the liquid phase. *Microporous Mesoporous Mater.* **2001**, *44*, 581–586. [[CrossRef](#)]
55. Gu, Y.-Y.; Zhao, X.-H.; Zhang, G.-R.; Ding, H.-M.; Shan, Y.-K. Selective hydroxylation of benzene using dioxygen activated by vanadium–copper oxide catalysts supported on SBA-15. *Appl. Catal. A Gen.* **2007**, *328*, 150–155. [[CrossRef](#)]
56. Jourshabani, M.; Badiei, A.; Shariatnia, Z.; Lashgari, N.; Mohammadi Ziarani, G. Fe-supported SBA-16 type cage-like mesoporous silica with enhanced catalytic activity for direct hydroxylation of benzene to phenol. *Ind. Eng. Chem. Res.* **2016**, *55*, 3900–3908. [[CrossRef](#)]
57. Abbo, H.S.; Titinchi, S.J. Di-, tri- and tetra-valent ion-exchanged NaY zeolite: Active heterogeneous catalysts for hydroxylation of benzene and phenol. *Appl. Catal. A Gen.* **2009**, *356*, 167–171. [[CrossRef](#)]
58. Yang, J.-H.; Sun, G.; Gao, Y.; Zhao, H.; Tang, P.; Tan, J.; Lu, A.-H.; Ma, D. Direct catalytic oxidation of benzene to phenol over metal-free graphene-based catalyst. *Energy Environ. Sci.* **2013**, *6*, 793–798. [[CrossRef](#)]
59. Hu, L.; Wang, C.; Yue, B.; Chen, X.; He, H. Direct hydroxylation of benzene to phenol using H₂O₂ as an oxidant over vanadium-containing nitrogen doped mesoporous carbon catalysts. *RSC Adv.* **2016**, *6*, 87656–87664. [[CrossRef](#)]
60. Hu, L.; Wang, C.; Yue, B.; Chen, X.; He, H. Vanadium-containing mesoporous carbon and mesoporous carbon nanoparticles as catalysts for benzene hydroxylation reaction. *Mater. Today Commun.* **2017**, *11*, 61–67. [[CrossRef](#)]
61. Pezhman, A.; Badiei, A.; Koolivand, A.; Ziarani, G.M. Direct hydroxylation of benzene to phenol over Fe₃O₄ supported on nanoporous carbon. *Chin. J. Catal.* **2011**, *32*, 258–263.
62. Xu, J.; Jiang, Q.; Chen, T.; Wu, F.; Li, Y.-X. Vanadia supported on mesoporous carbon nitride as a highly efficient catalyst for hydroxylation of benzene to phenol. *Catal. Sci. Technol.* **2015**, *5*, 1504–1513. [[CrossRef](#)]
63. Wang, C.; Hu, L.; Wang, M.; Yue, B.; He, H. Cerium promoted Vg-C₃N₄ as highly efficient heterogeneous catalysts for the direct benzene hydroxylation. *R. Soc. Open Sci.* **2018**, *5*, 180371. [[CrossRef](#)]
64. Cao, T.; Cai, M.; Jin, L.; Wang, X.; Yu, J.; Chen, Y.; Dai, L. Amorphous Cr-doped gC₃N₄ as an efficient catalyst for the direct hydroxylation of benzene to phenol. *New J. Chem.* **2019**, *43*, 16169–16175. [[CrossRef](#)]
65. Yu, Z.-H.; Gan, Y.-L.; Xu, J.; Xue, B. Direct Catalytic Hydroxylation of Benzene to Phenol Catalyzed by FeCl₃ Supported on Exfoliated Graphitic Carbon Nitride. *Catal. Lett.* **2020**, *150*, 301–311. [[CrossRef](#)]
66. Tu, T.N.; Nguyen, H.T.; Nguyen, H.T.; Nguyen, M.V.; Nguyen, T.D.; Tran, N.T.; Lim, K.T. A new iron-based metal–organic framework with enhancing catalysis activity for benzene hydroxylation. *RSC Adv.* **2019**, *9*, 16784–16789. [[CrossRef](#)]
67. Zhang, T.; Zhang, D.; Han, X.; Dong, T.; Guo, X.; Song, C.; Si, R.; Liu, W.; Liu, Y.; Zhao, Z. Preassembly strategy to single Cu-N₃ sites in porous hollow carbonitride spheres for selective oxidation of benzene to phenol. *J. Am. Chem. Soc.* **2018**, *140*, 16936–16940. [[CrossRef](#)]
68. Ito, S.; Mitarai, A.; Hikino, K.; Hirama, M.; Sasaki, K. Deactivation reaction in the hydroxylation of benzene with Fenton’s reagent. *J. Org. Chem.* **1992**, *57*, 6937–6941. [[CrossRef](#)]

69. Bal, R.; Tada, M.; Sasaki, T.; Iwasawa, Y. Direct phenol synthesis by selective oxidation of benzene with molecular oxygen on an interstitial-N/Re cluster/zeolite catalyst. *Angew. Chem. Int. Ed.* **2006**, *118*, 462–466. [\[CrossRef\]](#)
70. Xia, H.; Sun, K.; Sun, K.; Feng, Z.; Li, W.X.; Li, C. Direct spectroscopic observation of Fe (III)—Phenolate complex formed from the reaction of benzene with peroxide species on Fe/ZSM-5 at room temperature. *J. Phys. Chem. C* **2008**, *112*, 9001–9005. [\[CrossRef\]](#)
71. Borah, P.; Ma, X.; Nguyen, K.T.; Zhao, Y. A vanadyl complex grafted to periodic mesoporous organosilica: A green catalyst for selective hydroxylation of benzene to phenol. *Angew. Chem. Int. Ed.* **2012**, *124*, 7876–7881. [\[CrossRef\]](#)
72. Chen, P.; Chen, L.; Zeng, Y.; Ding, F.; Jiang, X.; Liu, N.; Au, C.-T.; Yin, S.-F. Three-dimension hierarchical heterostructure of CdWO₄ microrods decorated with Bi₂WO₆ nanoplates for high-selectivity photocatalytic benzene hydroxylation to phenol. *Appl. Catal. B Environ.* **2018**, *234*, 311–317. [\[CrossRef\]](#)
73. Chen, X.; Zhang, J.; Fu, X.; Antonietti, M.; Wang, X. Fe-g-C₃N₄-catalyzed oxidation of benzene to phenol using hydrogen peroxide and visible light. *J. Am. Chem. Soc.* **2009**, *131*, 11658–11659. [\[CrossRef\]](#)
74. Sannino, D.; Vaiano, V.; Isupova, L.A.; Ciambelli, P. Photo-Fenton oxidation of acetic acid on supported LaFeO₃ and Pt/LaFeO₃ perovskites. *Chem. Eng. Trans.* **2011**, *25*, 1013–1018. [\[CrossRef\]](#)
75. Zhang, P.; Gong, Y.; Li, H.; Chen, Z.; Wang, Y. Selective oxidation of benzene to phenol by FeCl₃/mpg-C₃N₄ hybrids. *RSC Adv.* **2013**, *3*, 5121–5126. [\[CrossRef\]](#)
76. Ohkubo, K.; Kobayashi, T.; Fukuzumi, S. Direct oxygenation of benzene to phenol using quinolinium ions as homogeneous photocatalysts. *Angew. Chem. Int. Ed.* **2011**, *123*, 8811–8814. [\[CrossRef\]](#)
77. Gu, Y.; Li, Q.; Zang, D.; Huang, Y.; Yu, H.; Wei, Y. Light-Induced Efficient Hydroxylation of Benzene to Phenol by Quinolinium and Polyoxovanadate-Based Supramolecular Catalysts. *Angew. Chem. Int. Ed.* **2020**. [\[CrossRef\]](#)
78. Ciambelli, P.; Sannino, D.; Palma, V.; Vaiano, V.; Eloy, P.; Dury, F.; Gaigneaux, E.M. Tuning the selectivity of MoOx supported catalysts for cyclohexane photo oxidehydrogenation. *Catal. Today* **2007**, *128*, 251–257. [\[CrossRef\]](#)
79. Sannino, D.; Vaiano, V.; Ciambelli, P.; Carotenuto, G.; Di Serio, M.; Santacesaria, E. Enhanced performances of grafted VOx on titania/silica for the selective photocatalytic oxidation of ethanol to acetaldehyde. *Catal. Today* **2013**, *209*, 159–163. [\[CrossRef\]](#)
80. Sannino, D.; Vaiano, V.; Ciambelli, P.; Hidalgo, M.C.; Murcia, J.J.; Navío, J.A. Oxidative dehydrogenation of ethanol over Au/TiO₂ photocatalysts. *J. Adv. Oxid. Technol.* **2012**, *15*, 284–293. [\[CrossRef\]](#)
81. Vaiano, V.; Sarno, G.; Sacco, O.; Sannino, D. Degradation of terephthalic acid in a photocatalytic system able to work also at high pressure. *Chem. Eng. J.* **2017**, *312*, 10–19. [\[CrossRef\]](#)
82. Fessi, N.; Nsib, M.F.; Cardenas, L.; Guillard, C.; Dappozze, F.; Houas, A.; Parrino, F.; Palmisano, L.; Ledoux, G.; Amans, D.; et al. Surface and Electronic Features of Fluorinated TiO₂ and Their Influence on the Photocatalytic Degradation of 1-Methylnaphthalene. *J. Phys. Chem. C* **2020**, *124*, 11456–11468. [\[CrossRef\]](#)
83. Žerjav, G.; Scandura, G.; Garlisi, C.; Palmisano, G.; Pintar, A. Sputtered vs. sol-gel TiO₂-doped films: Characterization and assessment of aqueous bisphenol A oxidation under UV and visible light radiation. *Catal. Today* **2020**, *357*, 380–391. [\[CrossRef\]](#)
84. Sclafani, A.; Herrmann, J. Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions. *J. Phys. Chem.* **1996**, *100*, 13655–13661. [\[CrossRef\]](#)
85. Vaiano, V.; Sacco, O.; Sannino, D.; Stoller, M.; Ciambelli, P.; Chianese, A. Photocatalytic removal of phenol by ferromagnetic N-TiO₂/SiO₂/Fe₃O₄ nanoparticles in presence of visible light irradiation. *Chem. Eng. Trans.* **2016**, *47*, 235–240. [\[CrossRef\]](#)
86. Devaraji, P.; Jo, W.-K. Noble metal free Fe and Cr dual-doped nanocrystalline titania (Ti_{1-x-y}M_{x+y}O₂) for high selective photocatalytic conversion of benzene to phenol at ambient temperature. *Appl. Catal. A Gen.* **2018**, *565*, 1–12. [\[CrossRef\]](#)
87. Gupta, N.; Bansal, P.; Pal, B. Metal ion-TiO₂ nanocomposites for the selective photooxidation of benzene to phenol and cycloalkanol to cycloalkanone. *J. Exp. Nanosci.* **2015**, *10*, 148–160. [\[CrossRef\]](#)
88. Shiraishi, Y.; Saito, N.; Hirai, T. Adsorption-driven photocatalytic activity of mesoporous titanium dioxide. *J. Am. Chem. Soc.* **2005**, *127*, 12820–12822. [\[CrossRef\]](#)

89. Yuzawa, H.; Aoki, M.; Otake, K.; Hattori, T.; Itoh, H.; Yoshida, H. Reaction mechanism of aromatic ring hydroxylation by water over platinum-loaded titanium oxide photocatalyst. *J. Phys. Chem. C* **2012**, *116*, 25376–25387. [CrossRef]
90. Ide, Y.; Nakamura, N.; Hattori, H.; Ogino, R.; Ogawa, M.; Sadakane, M.; Sano, T. Sunlight-induced efficient and selective photocatalytic benzene oxidation on TiO₂-supported gold nanoparticles under CO₂ atmosphere. *Chem. Commun.* **2011**, *47*, 11531–11533. [CrossRef]
91. Tomita, O.; Abe, R.; Ohtani, B. Direct synthesis of phenol from benzene over platinum-loaded tungsten (VI) oxide photocatalysts with water and molecular oxygen. *Chem. Lett.* **2011**, *40*, 1405–1407. [CrossRef]
92. Tanarungsun, G.; Kiatkittipong, W.; Assabumrungrat, S.; Yamada, H.; Tagawa, T.; Praserttham, P. Multi transition metal catalysts supported on TiO₂ for hydroxylation of benzene to phenol with hydrogen peroxide. *J. Ind. Eng. Chem.* **2007**, *13*, 870–877.
93. Devaraji, P.; Jo, W.-K. Natural leaf-assisted dual-phase two-dimensional leaf TiO₂ and Cu(OH)₂ co-catalyst for photocatalytic conversion of benzene to phenol. *Mater. Res. Bull.* **2019**, *110*, 67–75. [CrossRef]
94. Zhang, Y.; Park, S.-J. Stabilizing CuPd bimetallic alloy nanoparticles deposited on holey carbon nitride for selective hydroxylation of benzene to phenol. *J. Catal.* **2019**, *379*, 154–163. [CrossRef]
95. Verma, S.; Nasir Baig, R.; Nadagouda, M.N.; Varma, R.S. Hydroxylation of Benzene via C–H activation using bimetallic CuAg@g-C₃N₄. *ACS Sustain. Chem. Eng.* **2017**, *5*, 3637–3640. [CrossRef] [PubMed]
96. Shiravand, G.; Badii, A.; Ziarani, G.M.; Jafarabadi, M.; Hamzehloo, M. Photocatalytic synthesis of phenol by direct hydroxylation of benzene by a modified nanoporous silica (LUS-1) under sunlight. *Chin. J. Catal.* **2012**, *33*, 1347–1353. [CrossRef]
97. Ye, X.; Cui, Y.; Qiu, X.; Wang, X. Selective oxidation of benzene to phenol by Fe-CN/TS-1 catalysts under visible light irradiation. *Appl. Catal. B Environ.* **2014**, *152*, 383–389. [CrossRef]
98. Wang, D.; Wang, M.; Li, Z. Fe-based metal–organic frameworks for highly selective photocatalytic benzene hydroxylation to phenol. *ACS Catal.* **2015**, *5*, 6852–6857. [CrossRef]
99. Dasireddy, V.D.; Likozar, B. Selective photocatalytic oxidation of benzene to phenol using carbon nanotube (CNT)-supported Cu and TiO₂ heterogeneous catalysts. *J. Taiwan Inst. Chem. Eng.* **2018**, *82*, 331–341. [CrossRef]
100. Li, J.; Xu, Y.; Ding, Z.; Mahadi, A.H.; Zhao, Y.; Song, Y.-F. Photocatalytic selective oxidation of benzene to phenol in water over layered double hydroxide: A thermodynamic and kinetic perspective. *Chem. Eng. J.* **2020**, *388*, 124248. [CrossRef]
101. Bui, T.D.; Kimura, A.; Higashida, S.; Ikeda, S.; Matsumura, M. Two routes for mineralizing benzene by TiO₂-photocatalyzed reaction. *Appl. Catal. B Environ.* **2011**, *107*, 119–127. [CrossRef]
102. Devaraji, P.; Sathu, N.K.; Gopinath, C.S. Ambient oxidation of benzene to phenol by photocatalysis on Au/TiO₂. *ACS Catal.* **2014**, *4*, 2844–2853. [CrossRef]
103. Einaga, H.; Ibusuki, T.; Futamura, S. Improvement of catalyst durability by deposition of Rh on TiO₂ in photooxidation of aromatic compounds. *Environ. Sci. Technol.* **2004**, *38*, 285–289. [CrossRef]
104. Nishikawa, M.; Shiroishi, W.; Honghao, H.; Suizu, H.; Nagai, H.; Saito, N. Probability of Two-Step Photoexcitation of Electron from Valence Band to Conduction Band through Doping Level in TiO₂. *J. Phys. Chem. A* **2017**, *121*, 5991–5997. [CrossRef] [PubMed]
105. Choi, W.; Termin, A.; Hoffmann, M.R. The role of metal ion dopants in quantum-sized TiO₂: Correlation between photoreactivity and charge carrier recombination dynamics. *J. Phys. Chem.* **2002**, *98*, 13669–13679. [CrossRef]
106. Kunai, A.; Hata, S.; Ito, S.; Sasaki, K. The role of oxygen in the hydroxylation reaction of benzene with Fenton's reagent. Oxygen 18 tracer study. *J. Am. Chem. Soc.* **1986**, *108*, 6012–6016. [CrossRef] [PubMed]
107. Bui, T.D.; Kimura, A.; Ikeda, S.; Matsumura, M. Determination of oxygen sources for oxidation of benzene on TiO₂ photocatalysts in aqueous solutions containing molecular oxygen. *J. Am. Chem. Soc.* **2010**, *132*, 8453–8458. [CrossRef]

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