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Studies on vanadium catalyzed direct hydroxylation of aromatic hydrocarbons using hydrogen peroxide as oxidant

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ABSTRACT

Direct hydroxylation of aromatic hydrocarbons, *viz.* benzene, toluene and anisole to phenol, cresols and methoxyphenols respectively has been studied by using hydrogen peroxide as oxidant and vanadium based systems such as vanadyl tetraphenoxyphthalocyanine, $VO(acac)_2$, 20% V_2O_5/Al_2O_3, 14% V_2O_5/TiO_2, 11% V_2O_5/ZiO_2 as catalysts in acetonitrile under biphasic reaction conditions. Among the various vanadium-based catalysts studied, vanadyl tetraphenoxyphthalocyanine (VOPc) was found to be best from conversion as well as selectivity for hydroxy compounds points of view. The effect of various reaction parameters such as H_2O_2/substrate molar ratio, reaction temperature, solvent and catalyst concentration was systematically studied.

1. Introduction

Hydroxyaromatic compounds are valuable organic intermediates in chemical industries related to resin, plastics, pharmaceuticals and agrochemicals. Phenol for example is further processed to form phenol resins, caprolactam, bisphenol A, adipic acid. Similarly cresols are used for preparing antioxidants, herbicides, insecticides, dyes, flavoring agents, plastics and lubricating oils. In addition, *p*-cresol is particularly used for producing BHT (2,6-di-*tert*-butyl-4-hydroxytoluene) which is an important antioxidant. Guaiacol (*o*-methoxyphenol) and *p*-methoxyphenol also find extensive applications in the realm of pharmaceuticals, synthetic perfumes, antioxidants and polymerization inhibitors. World wide industrial production of phenol is done by using the Cumene process, which constitute a three step process and suffer from many disadvantages such as the lower conversion and formation of acetone as inevitable side product [1]. Cresols are primarily produced from toluene by multistep reaction sequence involving sulphonation, chlorination or by vapor phase methylation of phenol followed by the isolation of individual isomers by traditional distillation or crystallization [2,3]. Nevertheless, these processes suffer from the drawbacks like low yield of *p*-cresol, production of byproducts such as tolyl cresols and tolyl ethers. On the other hand, the vapor phase methylation of phenol yields only *o*-cresol and 2,6-xylenol albeit uses relatively expensive starting material phenol and require high capital cost. Similarly, guaiacol (*o*-hydroxy anisole) industrial process involves methylation of catechol with dimethyl sulphate or carbonate in presence of alkali and *p*-methoxyphenol is manufactured by selective methylation of hydroquinone with dimethyl sulphate or carbonate, however, both these processes are highly environmentally unacceptable [4].

The one step process for direct hydroxylation of aromatic hydrocarbons has therefore attracted world wide attention and is one of the most challenging issues in catalysis research at present. There are three main approaches known in the literature for the direct hydroxylation of benzene to phenol. First approach involves a gas phase hydroxylation of benzene with nitrous oxide over Fe-ZSM-5 zeolite at elevated temperatures [5–9], and the limitations associated with this process are the rapid deactivation of the catalyst due to coke formation, limited availability of oxidant N_2O and lower selectivity for phenol formation [10]. Second approach involves catalytic oxidation of benzene employing molecular oxygen as oxidant both in gas, liquid phases which suffers form the disadvantages like low conversion and poor selectivity for phenol [11–15]. The third approach which is being extensively studied is the catalytic hydroxylation of benzene using hydrogen peroxide as oxidant in presence of transition metal based catalysts like TS-1 [16,17], $Fe(DDC)_3$ [18,19], Fe/Ce mixed oxide [20].

Although hydroxylation of benzene to phenol has been extensively studied in the recent past, very little is known about the direct hydroxylation of toluene and anisole. Recently, Kumar et al. reported the direct hydroxylation of aromatics such as benzene, toluene and anisole to phenol, cresols and methoxyphenols respectively with enhanced reaction rates under solvent free

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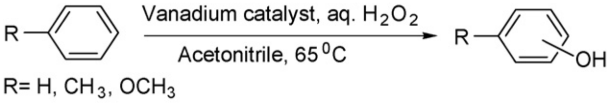

Scheme 1.

triphasic conditions using TS-1 as catalyst and H_2O_2 as oxidant [21].

Vanadium complexes and oxides due to their high reactivity and remarkable stability have emerged as efficient catalysts for a variety of oxidation reactions using hydrogen peroxide as oxidant [22–25], but there are scanty literature reports on the hydroxylation of aromatics [26–31]. This prompted us to report our findings on direct hydroxylation of aromatics, *viz.* benzene, toluene, anisole to phenol, cresols and methoxyphenols respectively using different vanadium-based heterogeneous catalysts such as vanadyl tetraphenoxyphthalocyanine, 20% V_2O_5/Al_2O_3, 14% V_2O_5/TiO_2, 11% V_2O_5/ZrO_2 and compare their catalytic efficiencies with homogeneous vanadyl acetylacetonate using hydrogen peroxide as oxidant in acetonitrile (Scheme 1).

2. Experimental

2.1. General

Vanadyl acetylacetonate and vanadyl tetraphenoxyphthalocyanine (purity 98%) were purchased from Aldrich and used as received. A 20% V_2O_5/Al_2O_3 catalyst was prepared on a γ-Al_2O_3 support (BET surface area 160 m^2/g) by an incipient wetness impregnation technique following the literature procedure [32]. The prepared catalyst was first dried at 110 °C (over night) and finally calcined at 500 °C for 4 h. Similarly 14% V_2O_5/TiO_2 and 11% V_2O_5/ZrO_2 catalysts were prepared on rutile TiO_2 support (surface area 33 m^2/g) and zirconia support (surface area 35 m^2/g) by using incipient wetness impregnation method [33–34]. The vanadium content of the prepared catalysts was estimated by ICP-AES (PS-3000 UV, Leeman labs). The catalysts were characterized by XRD, TPD, oxygen chemisorptions, nitrogen adsorption–desorption isotherm at liquid nitrogen temperature and the determined values were found to be in agreement with the literature values. Hydroxylation reactions were carried out in a glass round-bottomed flask in a batch manner.

2.2. Typical experimental procedure

To a 150-ml round-bottomed double-necked flask containing benzene (0.05 mol, 3.9 g), 50% aq. hydrogen peroxide (0.25 mol, 17.0 g) and acetonitrile (50 ml) was added vanadyl tetraphenoxyphthalocyanine (2.5 mol%, 1.18 g) and the reaction was continued with vigorous stirring at 65 °C for 8 h. After completion, the catalyst was separated by simple filtration through a Buckner funnel and the filtrate so obtained was passed through a short column of silica gel and thoroughly washed with acetonitrile. The resulting mixture was concentrated under reduced pressure and the obtained residue was analyzed by high resolution GCMSD, EI, quadrapole mass analyzer, EM detector. The conversion of benzene to phenol was determined on the basis of the weight of the residue left after evaporation and selectivity for phenol formation was determined by GCMSD. Further these data were found to match well with the conversion and selectivity values obtained by direct analysis of the reaction mixture by GCMSD using *o*-cresol as internal standard. Similarly hydroxylation of toluene and anisole was carried out under same reaction conditions. In case of hydroxylation of anisole, both the conversion as well as selectivity was determined by GC-MSD.

3. Results and discussion

At first to compare the catalytic efficiency of various heterogeneous vanadium-based catalysts such as vanadyl tetraphenoxyphthalocyanine, 20% V_2O_5/Al_2O_3, 14% V_2O_5/TiO_2, 11% V_2O_5/ZrO_2 with homogeneous vanadyl acetylacetonate we carried out the hydroxylation of benzene, toluene and anisole to phenol, cresols and hydroxylanisoles respectively with aqueous hydrogen peroxide as oxidant in a molar ratio 1:1 under vigorous stirring at 65 °C for 8 h using acetonitrile as solvent. These results are presented in Tables 1–3. Among the different vanadium-based

Table 1
Comparison of various vanadium-based catalysts for direct hydroxylation of benzene to phenol with hydrogen peroxide[a]

Entry	Catalyst	Conv. (mol%)	Selectivity of products (%)[b]		
			Phenol	Benzoquinone	Unidentified
1	$VO(acac)_2$	11	100	–	–
2	Vanadyl tetraphenoxyphthalocyanine	22.4	100	–	–
3	20% V_2O_5/Al_2O_3	10	93	–	7
4	14% V_2O_5/TiO_2	5	91	–	9
5	11% V_2O_5/ZrO_2	7	92	0.5	7.5

[a] Reaction conditions: benzene (0.05 mol), catalyst (2.5 mol%), temperature. (65 °C), reaction time (8 h), H_2O_2/benzene molar ratio (1:1), acetonitrile (20 ml).
[b] Products were analyzed using GCMSD, EI quadrapole mass analyzer, EM detector.

Table 2
Comparison of various vanadium-based catalysts for hydroxylation of toluene using aqueous hydrogen peroxide as oxidant and acetonitrile as solvent[a]

Entry	Catalyst	Conv. (mol%)	Product selectivity[b]		
			o-Cresol (%)	*m,p*-Cresol (%)	Unidentified (%)
1	$VO(acac)_2$	5	37	56	7
2	Vanadyl tetraphenoxyphthalocyanine	18.74	38	57	5
3	20% V_2O_5/Al_2O_3	4	20	68	12
4	14% V_2O_5/TiO_2	2	18	72	10
5	11% V_2O_5/ZrO_2	2	19	70	11

[a] Reaction conditions: toluene (0.05 mol), catalyst (2.5 mol%), temperature. (65 °C), reaction time (8 h), H_2O_2/toluene molar ratio (1:1), acetonitrile (20 ml).
[b] Products were analyzed using GCMSD, EI quadrapole mass analyzer, EM detector.

Table 3
Comparison of various vanadium-based catalysts for hydroxylation of anisole using aqueous hydrogen peroxide as oxidant and acetonitrile as solvent[a]

Entry	Catalyst	Conv. (mol%)	Product selectivity[b]		
			o- (%)	p- (%)	Unidentified (%)
1	$VO(acac)_2$	2	–	26	74
2	Vanadyl tetraphenoxyphthalocyanine	6	–	47	53
3	20% V_2O_5/Al_2O_3	–	–	–	–
4	14% V_2O_5/TiO_2	–	–	–	–
5	11% V_2O_5/ZrO_2	–	–	–	–

[a] Reaction conditions: anisole (0.05 mol), catalyst (2.5 mol%), temperature. (65 °C), reaction time (8 h), H_2O_2/anisole molar ratio (1:1), acetonitrile (20 ml).
[b] Products were analyzed using GCMSD, EI quadrapole mass analyzer, EM detector.

Table 4
Effect of various reaction parameters on hydroxylation of aromatics using vanadyl tetraphenoxyphthalocyanine as catalyst and acetonitrile as solvent[a]

Entry	Substrate	H_2O_2/substrate mole ratio	Temperature (°C)	Conv. (mol%)	Selectivity of products (%)[b]			
					p-	o-	Unidentified	Phenol
1	Benzene	1	65	22.40	–	–	–	100
2		2		33.19	–	–	–	100
3		5		41.49	–	–	–	100
4	Toluene	1	65	18.74	57[c]	38	5	–
5		2		28.90	54[c]	40	6	–
6		5		34.90	55[c]	36	9	–
7	Anisole	1	65	6.20	47	-	53	–
8		2		11.00	52		48	–
9		5		18.00	45		55	–
10	Benzene	5	25	25.00	–	–	–	100
11			80	48.00	–	–	15	65
12	Toluene	5	25	25.00	55[c]	38	7	–
13			80	39.00	42[c]	32	26	–
14	Anisole	5	25	11.00	48	–	52	–
15			80	22.00	39	–	61	–

[a] Reaction conditions: catalyst (2.5 mol%), temperature (65 °C), reaction time (8 h), substrate (0.05 mol).
[b] Products were analyzed using GCMSD, EI quadrapole mass analyzer, EM detector.
[c] Mixture of *m*/*p*-isomers.

catalysts studied vanadyl tetraphenoxyphthalocyanine (VOPc) was found to be most efficient from conversion and selectivity of desired products view points. Further studies for hydroxylation of benzene, toluene, and anisole with aqueous hydrogen peroxide were carried out by using this catalyst.

To evaluate the effect of reaction parameters such as H_2O_2/substrate molar ratio and temperature we carried out the hydroxylation of benzene, toluene and anisole with hydrogen peroxide using vanadyl tetraphenoxyphthalocyanine as catalyst under similar reaction conditions, these results are summarized in Table 4. In all cases the conversion of the aromatics to corresponding hydroxyl aromatics was found to increase with increasing the molar ratio of H_2O_2/substrate from 1 to 5 (Table 4, entries 1–9). It was interesting to note that even at higher conversion (41.49 mol% for benzene to phenol), selectivity of phenol remained 100% and there was no evidence for the formation of any other product like hydroquinone or benzoquinone. Hydroxylation of toluene yielded *o*- and *m*/*p*-cresols with *m*/*p*-cresol being formed predominantly. Hydroxylation of anisole showed maximum conversion 18 mol% with the formation of *p*-hydroxyanisole as main product. Some unidentified products were also observed during the hydroxylation of toluene and anisole (Table 4, entries 4–9). We also estimated the amount of left over hydrogen peroxide in case of hydroxylation of benzene by iodometric titration and did not found unreacted hydrogen peroxide at the end of the reaction. The selectivity for the formation of phenol based on H_2O_2 with H_2O_2/benzene molar ratio 1 and 5 were found to be 22.4 and 8.3%, respectively. Hydroxylation of benzene, toluene and anisole was found to be slow at room temperature, affording lower conversions to corresponding hydroxyl aromatics (Table 4, entries 10, 12, 14). However at higher reaction temperature that is 80 °C, although the conversions were found to increase but selectivity for desired products remained comparatively lower with the increased formation of unidentified products (Table 4, entries 11, 13, 15).

To evaluate the effect of solvent we studied the hydroxylation of benzene with H_2O_2 in a molar ration 1:1 in presence of vanadyl tetraphenoxyphthalocyanine as catalyst using different solvents as reaction media under described reaction condition (Table 5). Among the various solvents such as acetonitrile, acetone, methanol and water studied, acetonitrile was found to be most promising from both conversion of benzene and selectivity for phenol points of view. To evaluate the effect of catalyst concentration, we carried out the hydroxylation of benzene by varying the amount of catalyst under same reaction conditions. During this course, we observed

Table 5
Effect of various solvents on hydroxylation of benzene with hydrogen peroxide using vanadyl tetraphenoxyphthalocyanine as catalyst[a]

Entry	H_2O_2/benzene molar ratio	Solvent	Conversion (mol%)	Phenol selectivity (%)
1	1:1	Acetonitrile	22.4	100
2	1:1	Acetone	7.0	80
3	1:1	Methanol	4.0	40
4	1:1	Water	10.0	60

[a] Reaction condition: benzene (0.05 mol), vanadyl tetraphenoxyphthalocyanine (2.5 mol%), temperature (65 °C), reaction time (8 h).

Table 6
Effect of catalyst concentration on hydroxylation of benzene using vanadyl tetraphenoxyphthalocyanine as catalyst[a]

Entry	H_2O_2/benzene molar ratio	Catalyst conc. (mol%)	Conversion (mol%)	Phenol selectivity (%)
1	1:1	2	20.0	100
2	1:1	2.5	22.4	100
3	1:1	5	23.0	100
4	1:1	10	25.0	100

[a] Reaction condition: benzene (0.05 mol), acetonitrile (20 ml), temperature (65 °C), reaction time (8 h).

Table 7
Results of recyclability experiments for hydroxylation of benzene to phenol using vanadyl tetraphenoxyphthalocyanine as catalyst[a]

Run	H_2O_2/benzene molar ratio	Conv. (mol%)	Phenol selectivity (%)
1	1:1	22.4	100
2	1:1	22.4	100
3	1:1	22.2	100
4	1:1	22.2	100

[a] Reaction condition: vanadyl tetraphenoxyphthalocyanine (2.5 mol%), acetonitrile (20 ml), temperature (65 °C), reaction time (8 h).

only marginal difference in conversion of benzene to phenol with increasing the catalyst concentration from 2 to 10 mol% (Table 6). While increase in the catalyst concentration from 2.0 to 2.5 mol%, the conversion of benzene to phenol increased from 20 to 22.4%, however further increase in catalyst concentration up to 10 mol% the conversion of benzene increased marginally to 25%.

Next we checked the recyclability of the vanadyl tetraphenoxyphthalocyanine for hydroxylation of benzene with hydrogen peroxide in a molar ration 1:1 under similar reaction conditions. After completion of the reaction the catalyst was separated by filtration and reused as such for subsequent hydroxylation of benzene (for three runs) after adding fresh substrate and oxidant (50% H_2O_2). In these experiments conversion as well as selectivity for phenol remained almost same (Table 7). Importantly no metal leaching was observed in this course as ascertained by ICP-AES, indicating that the reaction is truly heterogeneous in nature.

Although the exact mechanism of the reaction is not clear at this stage however in analogy to the existing mechanism for hydroxylation of benzene by vanadyl (IV) complexes [35,36], the mechanistic pathway for vanadyl tetraphenoxyphthalocyanine probably involves the conversion of vanadyl (IV) species to vanadyl (V) oxo-peroxo species in presence of H_2O_2 which acts as a hydroxylation species.

4. Conclusion

In summary, we have developed a simple yet efficient methodology for the direct hydroxylation of benzene to phenol, toluene to cresols and anisole to methoxy phenols with aqueous hydrogen peroxide as oxidant using vanadyl tetraphenoxyphthalocyanine as catalyst, acetonitrile as solvent under mild reaction conditions. The catalyst could be easily recovered from the reaction mixture by simple filtration and reused for subsequent four runs without loss in catalytic activity. The important advantages such as higher conversions with improved selectivity for hydroxy products (for example 100% selectivity for phenol even at high conversion), mild reaction condition, heterogeneous nature and high efficiency, versatility and recyclability of the catalyst make the developed protocol an environmentally benign alternative to the existing methods for hydroxylation of aromatic hydrocarbons.

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