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Cetyl Alcohol Mediated Synthesis of $CuCr_2O_4$ Spinel Nanoparticles: A Green Catalyst for Selective Oxidation of Aromatic C-H Bonds with Hydrogen Peroxide

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We report here cetyl alcohol-promoted synthesis of spherical $CuCr_2O_4$ spinel nanoparticles with almost uniform morphology, prepared hydrothermally. Detailed characterization of the material was carried out by XRD, XPS, ICP-AES, SEM, TEM, and TGA. XRD revealed the exclusive formation of $CuCr_2O_4$ spinel phase and TEM showed the formation of 20-40 nm particle size. The catalyst was highly active for selective oxidation of benzene to phenol with H_2O_2. The influence of reaction parameters were investigated in detail. The catalyst was found to be selective for hydroxylation other aromatic alkanes as well. The reusability of the catalyst was tested by conducting same experiments with the spent catalyst and it was found that the catalyst does not show any significant activity loss even after 5 reuses. The benzene conversion of 67% with 94% phenol selectivity was achieved at 75 ºC temperature.

Direct functionalization of C-H bonds has been developed as a powerful strategy to form new chemical bonds.[1] Among them, transition-metal-catalyzed hydroxylation of C-H bond has drawn considerable attention because of the industrially important alcohol or phenol products. Inspite of the significant development in the past decades, catalytic hydroxylation of C_{sp2}-H bonds still remains a very challenging task. Selective oxidation of inactive hydrocarbons to industrially important intermediates still remains a major challenge.[2] Among these oxygenates, phenol is the most desirable and value-added product due to its widespread use in the fields of resin, plastics, pharmaceuticals, agrochemicals, etc. It is mainly used for the production of a large number of intermediates such as bisphenol, caprolactum, aniline, alkylphenol, chlorophenol, salicylic acid, etc., which are then further used to produce epoxy resin for paints, polycarbonate plastics for CDs and domestic appliances, nylon, polyamides, antioxidants, surfactants, detergents, anticeptics, medicines etc.[3] Industrially, phenol is produced by cumene process. The cumene process is performed by first the reaction of benzene with propene on acid catalysts such as MCM-22, second auto-oxidation of the obtained cumene to form explosive cumene hydroperoxide, and finally the decomposition of cumene hydroperoxide to phenol and acetone in sulfuric acid.[4] Apart from multistep nature, this process suffers from low yield (~5% based on the amount of benzene initially used) and produces explosive intermediate, cumene hydroperoxide and by-products. So, the one-step process for the direct conversion of benzene to phenol is an area of great potential interest. Although there have been several reports using different oxidizing agents like N_2O,[5] H_2O_2,[6] NH_3+ O_2,[7] air+CO[8] etc. however, the selectivity of phenol is rather poor, since phenol is more reactive towards oxidation than benzene itself and substantial formation of over-oxygenated by-products (catechol, hydroquinone, benzoquinones and tars) also occurs,[9] and rapid deactivation of the catalyst by coke deposition during gas phase reaction.[10] The use of H_2O_2 as oxidizing agent in liquid phase hydroxylation of benzene is of great advantage from both environmental and industrial viewpoint and thus recognized as "green oxidant".[11] Bianchi et al. have developed a water-acetonitrile biphasic reaction method in which $FeSO_4$, soluble in the aqueous medium, was used as catalyst and H_2O_2 as oxidant.[12] By employing this method, a significant selectivity to phenol (97%) was observed, although the benzene conversion was 8.6%. Zhang et al. reported a benzene conversion of 34.5 % with a selectivity of 100% towards the phenol using H_2O_2 as oxidant in a mixture of glacial acetic acid and acetonitrile, over Keggin-type molybdovanadophosphoric heteropoly acids.[13] Recently, Borah et. al reported a benzene conversion of 27% and a phenol selectivity of 100% over vanadyl-complex grafted on periodic mesoporous organosilica.[14] So far it is concern, apart from high yield of phenol, recyclability of the catalysts, product separation and maintaining efficiency of H_2O_2 are major issues in liquid phase benzene hydroxylation; therefore, production of phenol by direct hydroxylation of benzene in liquid phase with both high activity and selectivity using heterogeneous catalyst(s) that contain non-leachable species is of current interest. Thus, the direct and selective introduction of the hydroxyl group into the aromatic compounds, especially conversion of benzene to phenol, is one of the most challenging fields in oxidation chemistry today and therefore, regarded as one of the ten most challenges of catalysis.[2e,15]

Copper chromium mixed oxides with a spinel structure had been recognized as an important class of bi-metallic oxides that act as a versatile catalyst.[16] Apart from its usage in chemical industries, copper chromite finds its major application as a burn rate modifier in solid propellant processing for space launch vehicles globally.[17] The higher activity of copper chromite is attributed to the tetragonally distorted normal spinel structure with c/a < 1(where a and c are lattice constants in a unit cell along x and z axes respectively) and the arrangement of copper in its structure.[18] Although, a variety of synthetic methods have been employed in the preparation of Cu-Cr catalysts, yet controlled syntheses at large scale, with tunable morphology and its fruitful application in catalytic oxidation still remain a challenging task in the field of catalysis.

Herein, we report cationic surfactant cetyl alcohol-promoted synthesis of the preparation of $CuCr_2O_4$ nanoparticles spinel catalyst with 20-40 nm particle size. Although cetyl alcohol has been used in different purposes,[19] so far, there is no report of using cetyl alcohol as template for the preparation of spinel nanparticles, to the best of our knowledge. Here, we also report direct hydroxylation of benzene to phenol using the so prepared $CuCr_2O_4$ nanoparticles spinel catalyst and H_2O_2 as oxidant. A benzene conversion of 67% and phenol selectivity of 94% was achieved over this catalyst.

The $CuCr_2O_4$ nanoparticles spinel catalyst was prepared modifying our own synthetic method using nitrate precursors of copper and chromium and substituting CTAB by cetyl alcohol.[20] Although the mechanism for the formation of $CuCr_2O_4$ spinel nanoparticles promoted by cetyl alcohol is not very clear, we believe that this material served as modifier, that played an important role in the orchestrating the particle size. The catalyst was characterized by XRD, XPS, ICP-AES, SEM, TEM, TGA. The crystalline phase, degree of crystallinity and phase purity were determined by X-ray diffraction (XRD). The XRD patterns of the Cu-Cr catalysts are presented in Fig 1. showed the typical diffraction lines of the bulk, single phased tetragonal $CuCr_2O_4$ spinel [space group $I4_1$/amd, with lattice parameters : a (Å)= 6.03277(1); b (Å) = 6.03277(1); c (Å) = 7.78128(1)][21] exclusively with the maximum intensity peak at 2θ value of 35.16° (JCPDS. 05-0657; 21-874); no impurity phase was found such as $CuCrO_2$ and not even other phases of $CuCr_2O_4$ like cubic or monoclinic, which reflected the high purity of our synthetic procedure. By using the Scherrer equation, the average crystallite size (based on 35.16°) was found 28 nm. XRD diffractogram also predicts that, the catalyst retains its spinel phase even after 5 recycles. The surface composition of the catalyst was detected from XPS analysis (Fig. S1-S3, ESI†) which stated that copper is in the +2 oxidation state and chromium is in the +3 oxidation state which matched with the $CuCr_2O_4$ individual element's oxidation states. SEM images of the catalyst (Fig. 2a-c) showed the formation of almost homogeneously distributed uniform particles, whereas, that of commercial catalyst (Fig. S4) and prepared Cu-Cr catalyst without using cetyl alcohol (Fig. S5) showed formation of agglomerates and non-uniform particles. These results indicated the fact that, cetyl-alcohol plays an important role in orchestrating the $CuCr_2O_4$ spinel nanoparticles size. During synthesis-procedure, addition of cetyl alcohol probably formed micelle under alkaline medium and binded Cu and Cr ions and segregated in a spherical manner. Thus, after calcination, almost spherical $CuCr_2O_4$ spinel nanoparticles (with uniform morphology) were formed (confirmed from SEM). The attachment of cetyl alcohol on Cu and Cr surface was further confirmed from the TGA analysis of the uncalcined sample (Fig. S6).The TGA diagram showed that the weight loss occurs in three stages, first being the loss of water followed by the decomposition of reactants to form NO_x and organic phases at 150 to 250 °C and finally the combustion of cetyl alcohol between 250°–400 °C. A further small mass loss is noticed between 400°–550 °C due to the elimination of remaining carbon and organic compounds. No weight loss was observed when the temperature was further increased from 550° to 1000° C, indicating the stability of the catalyst (spinel phase) upto 1000° C. Total mass reduction of 34.4% confirmed the complete the removal of the template. The EDX analysis confirmed that the synthesized product was composed of Cu, Cr and O only (Fig. 2d), which indicated that, the template has been completely removed upon calcinations; furthermore, it also confirmed the purity of the synthetic procedure. Elemental mapping obtained from EDX analysis (based on Fig.2b) showed the coordinate-locations of Cu, Cr and O respectively (Fig. S7 b-d). A representative TEM image of the catalyst has been shown in Fig 3. The sizes of the particles estimated from TEM were in good agreement with those obtained from XRD. In the HRTEM image, distinct lattice fringes were clearly seen with a d-spacing of 0.30 nm corresponding to [220] plane of $CuCr_2O_4$ spinel[17a] with diffraction angle (2θ) of 29.6°. The TEM image of the spent catalyst (after 5 recycle) (Fig. 3d) revealed that the particle size of the $CuCr_2O_4$ spinel was almost unchanged during the catalysis.

It is a known fact that, in most transition metal-catalyzed oxidation systems, the C-H bond(s) adjacent to a π-system is hydroxylated selectively[11] and we explored benzene hydroxylation reaction in liquid phase using different catalysts of transition metals. In our previous report, we showed synthesis of cationic surfactant CTAB mediated synthesis of Cu (II) nanoclusters supported on nanocrystalline Cr_2O_3 catalyst, which effectively catalyzed the oxidation of cyclohexane at room temperature by activating C-H bond (sp^3 C atom) effectively.[20] We employed this catalyst in benzene hydroxylation reaction in liquid phase taking H_2O_2 as oxidant. Although the catalyst showed efficiency towards phenol selectivity (Table 1, entry 7), but it suffered severe leaching, waning the catalytic system. We therefore modified Cu: Cr molar ratio (taking 1:2) and prepared $CuCr_2O_4$ spinel nanoparticles catalyst, which is devoid of leaching properties.

The activities of $CuCr_2O_4$ spinel nanoparticles (Cu-Cr^{NP}) catalyst in the direct hydroxylation of benzene to phenol in liquid phase by using H_2O_2 as oxidant have been summarized in Table 1. Complete analyses showed that detected major product in the reaction mixture was phenol, with some catechol and 1, 4 benzoquinone as by-products. While optimizing the reaction conditions, we noticed that the yield of the desired product (i.e. phenol) increased by increasing the amount of H_2O_2 (Fig. S8, ESI†). However, the use of excess of oxidant (H_2O_2) did not meet the economy of chemical reactions at this temperature, due to the formation of over-oxidized products. Blank experiment was performed in absence of catalyst; conversion of benzene was too poor to be detected by GC analysis (Table 1, entry 10); this result reflected the necessity of the catalyst. Maintaining all the optimum conditions, when the reaction was allowed to run for hours, conversion of benzene with significant decrease in phenol selectivity was noticed (Fig. S9, ESI†). A decreasing trend for the H_2O_2 efficiency on increase in reaction time was also speculated, presumably because of self-decomposition nature of H_2O_2. Furthermore, polymerized phenol was also noticed in the reaction mixture after 24 hours. This may be a possible reason for the deactivation of the catalyst.

It is worth mentioning that, small amount of biphenyl was also discovered in the reaction mixture when excess amount of H_2O_2 was used. This phenomenon indicates the probable involvement of free-radical mechanism. The hypothesis was confirmed, when we used 2,6-di-*tert*-butyl-4-methyl phenol as a radical scavenger with benzene (10 wt% wrt benzene) was taken. No phenol was detected till 12h. We also observed that, the catalyst was active only in acetonitrile solvent. We believe that, Cu^{2+} in the catalyst framework interacts with the π-electron cloud of benzene and probably, the flexibility property of the Cu (II)-framework renders the catalytic system suitable for lowering the activation energy of the oxidation reaction.[22] Cr (III) is not involved in this reaction, but stabilizes Cu (II) ions against aggregation during reaction.[23] Probably, the high OSPE (octahedral site preference energy) for Cr (III) inhibits it to take part in the reaction,[24] thus the stable spinel framework remains uninterrupted and the oxidation reaction follows the "single site heterogeneous catalysis" path.[22] Cr^{3+} is not involved in the reaction but stabilizes the copper ion(s) against aggregation during the reaction condition.[23] H_2O_2 does not interact with benzene at normal condition. H_2O_2 dissociation is believed to occur homogeneously over the $CuCr_2O_4$ catalyst and follows the mechanism, suggested by Kazarnovsky.[25] Dissociation of H_2O_2 over $CuCr_2O_4$ generates the active species $^{\bullet}OH$ (free hydroxy radical).These hydroxy radicals participate as an electrophile in this reaction[26] which attacks the phenyl carbon atom by means of homolytic C–H bond cleavage mechanism, thereby produces phenol moiety on the surface of the catalyst. Use of excess H_2O_2 increases the dissociation rate, causing an increase of local pH;[27] consequently, generated excess $^{\bullet}OH$ radicals attack concomitantly the phenyl radical to produce biphenyl moiety, and thereby explains the presence of biphenyl in the reaction medium.

Notably, commercial Cr_2O_3, CuO, Cu_2O and $CuCr_2O_4$ catalyst did not show any good activity for phenol yield (Table 1, entry 1-4). Commercial $CuCr_2O_4$ catalyst did not show any activity. The reason can be attributed to the small size as well as extreme stable spinel phase, containing non-leachable species of the $CuCr_2O_4$spinel nanoparticles catalyst. The comparatively smaller size of $CuCr_2O_4$ spinel nanoparticles catalyst possess comparatively high specific surface area (65 m^2/g) which corresponds to higher dispersion of the catalyst that leads to the availability of more exposed surface active sites, where the catalytic reaction takes place in comparison to the commercial $CuCr_2O_4$ (with surface area 5 m^2/g). Inevitably, a higher reaction rate was observed in case of the $CuCr_2O_4$ spinel nanoparticles catalyst.

Conventional catalyst prepared by impregnation method also showed negligible activity (Table 1, entry 5). The concentrations of both components as found with ICP-AES were low and a hot filtered solution did not continue even when either $Cu(NO_3)_2$, $Cr(NO_3)_3$ or even the mixture of both were added in the reaction medium in absence of the catalyst.The corroboration of all these detailed to the conclusion that, nanoparticles of $CuCr_2O_4$ spinel, as well as acetonitrile medium is necessary for the benzene hydroxylation reaction. When n-octane and dimethylformamide (DMF) were used as solvents, the catalyst showed very poor activity. Although high phenol selectivity was achieved in these solvents, but the conversion of benzene was very less. This can be attributed to the fact that, n-octane is highly hydrophobic and DMF is highly hydrophilic in nature.[12]

The reusability test of the catalyst has been displayed in Table 2. After each run, a used catalyst was used several times by acetone and ethanol and kept at oven (120 °C) for 2 h and employed for the next run. We observed that the catalyst showed negligible change in its activity. After the catalyst had been used in 5 runs, significant change in the activity of the catalyst was hardly observed (Table 1, entry). XRD diffractogram of the used catalyst showed that the spinel phase was retained even after 5 reuses. The amount of Cu and Cr present in $CuCr_2O_4$ catalyst after 5 reuses was almost same as that in the fresh catalyst (estimated by ICP-AES) confirming the true heterogeneity of the catalyst.

In view of the above results, the catalytic system that renders the best yield in oxidation of benzene to phenol was applied in the subsequent studies. Various substituted benzenes were tested under this reaction conditions and the results are summarized in Table 3. Electron donor groups (-CH_3) favour the hydroxylation (Table 3, entry 1-3) in the phenyl ring. This may be attributed to the fact that, electron donor groups enhances electron density in the phenyl ring and welcome hydroxyl radicals (serve as electrophiles) to attack C-H bonds of phenyl ring to facilitate hydroxylation in the aromatic C-H bonds. In contrast, strongly electron withdrawing group (-Cl, -NO_2) prohibit the attack of hydroxyl radicals in the phenyl ring (Table 3, entry 4-6). Consequently, phenyl ring with strong electron-withdrawing groups showed very poor yield. Furthermore, *p*-hydroxy product was found as the main product in most of the cases, indicating the selective nature of the catalyst. We also noticed that, with the increment of branching of alkyl groups in the phenyl ring, oxidation in the side chain is favoured rather than hydroxylation in the phenyl ring; this may be attributed to well interaction of the exposed side chain with the catalyst.

Conclusions

In summary, we have reported cetyl alcohol-promoted simple preparation method to prepare 20-40 nm $CuCr_2O_4$ spinel nanoparticles having high thermal stability and good catalytic activity for the single step conversion of benzene to phenol using H_2O_2, exhibiting 67% benzene conversion and 94% selectivity towards phenol at 75 °C. The catalyst can be reused several times without any activity loss. The experimental findings form new basis for the structure-activity relationships of the copper-chromium catalysts in benzene to phenol hydroxylation chemistry, which reflects the prerequisites for a knowledge-based design of improved catalytic materials.The proposed method is also advantageous from the standpoint of low cost, environmental benignity and operational simplicity; furthermore, it can be applicable to large-scale reactions. This environmentally benign, "green" route to phenol production may be a potential alternative to the existing cumene process.

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Notes and references

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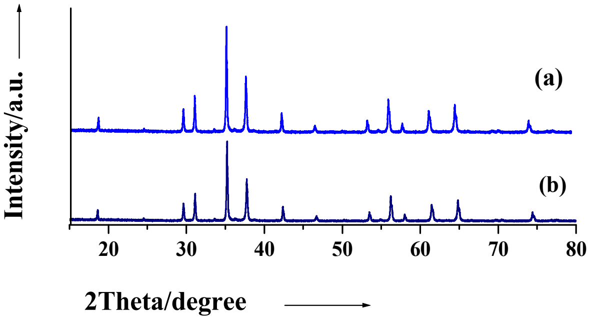


Fig. 1 XRD diffractogram of (a) fresh and (b) spent (after 5 reuses) of the $CuCr_2O_4$ nanoparticles catalyst.

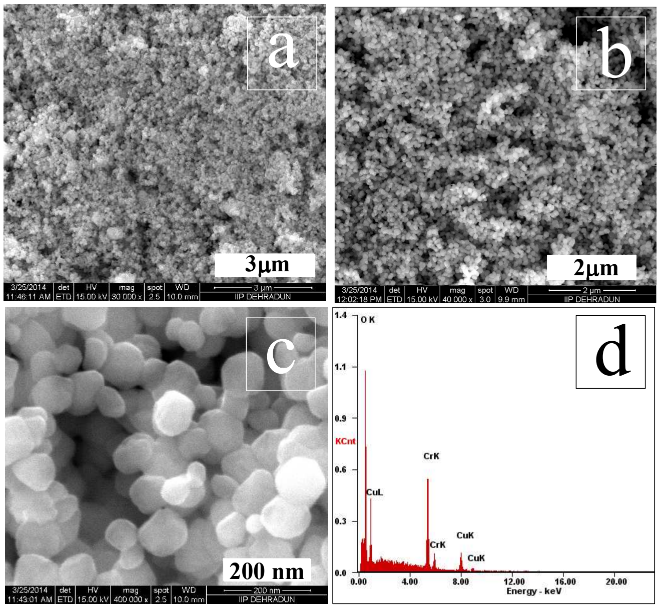


Fig. 2 SEM images (a-c) and (d) the SEM-EDAX image of the $CuCr_2O_4$ nanoparticles catalyst.

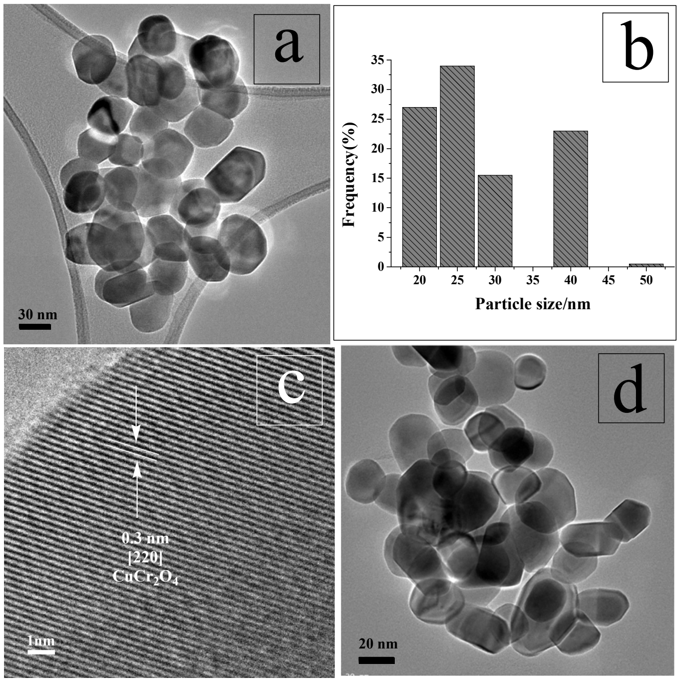


Fig. 3 (a) TEM image, (b) particle size distribution (histogram), (c) HRTEM of fresh and (d) TEM image of spent (after 5 recycles) $CuCr_2O_4$ nanoparticles catalyst.

Table 1. Reaction Conditions of Catalytic Oxidation of Benzene[a)]

Entry	Catalyst	C_B[b)] (%)	S_P[c)] (%)	Y_P[d)] (%)	E_o[e)] (%)
1	CuO^{COM}	5.5	5.5	0.3	0.06
2	Cu_2O^{COM}	6.8	8.0	0.5	0.1
3	$Cr_2O_3^{COM}$	7.5	2.0	0.1	0.03
4	$CuCr_2O_4^{COM}$	13.5	15.0	2	0.4
5	$CuO\text{-}Cr_2O_3^{IMP}$	12	15	1.8	0.4
6[f)]	$CuO\text{-}Cr_2O_3$	28	75	21	4.2
7[g)]	$CuCr_2O_4^{NP}$	67	94	62.9	12.6
8[h)]	$CuCr_2O_4^{NP}$	63.8	92	58.7	11.7
9[i)]	$CuCr_2O_4^{NP}$	-	-	-	-
10	No Catalyst	-	-	-	-

[a)] Typical reaction conditions: solvent (MeCN) = 10ml, substrate (benzene) = 1g, catalyst= 0.05g, benzene: H_2O_2 (molar ratio) = 1:5, reaction temperature = 75 °C; time = 12 h. [b]C_B = Conversion of benzene based upon the FID-GC using anisole as external standard = [Moles of benzene reacted/initial moles of benzene used] x 100. [c]S_P = Selectivity to phenol = [Moles of products produced/ moles of benzene reacted] x 100. [d]Y_P = Yield of phenol= $C_B \times S_P/100$. [e)] E_o = H_2O_2 efficiency = [Moles of phenol formed/total moles of H_2O_2

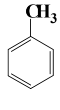
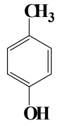
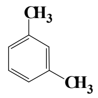
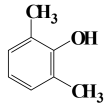
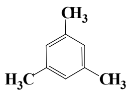
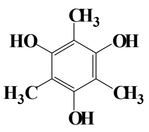
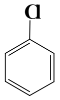
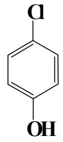
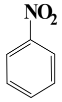
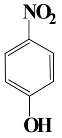
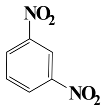
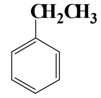
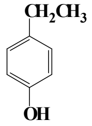
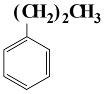
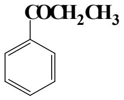
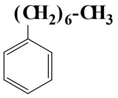
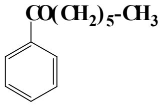
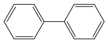
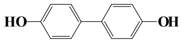
added]× 100. [f] Cu-nanoclusters supported on Cr_2O_3. [g] Prepared $CuCr_2O_4$ spinel nanoparticles and [h] catalyst after 5 reuse. [i] Using 2,6-di-*tert*-butyl-4-methyl phenol as radical scavanger. COM: commercial; IMP: impregnation method; CPM: co-precipitation method; NP: nanoparticles.

Table 2. Recyclability Tests of $CuCr_2O_4$ Spinel Nanoparticles Catalyst for the Hydroxylation of Benzene to Phenol.[a]

Recycling No.	C_B[b] (%)	S_P[c] (%)	Y_P[d] (%)
1	67	94	62.9
2	66.5	94	62.5
3	65.5	93.5	61.2
4	65.5	93	60.9
5	64	92.5	59.2
6	63.8	92	58.7

[a]Reaction Condition: solvent (MeCN) = 10 ml; benzene =1g; catalyst= 0.05g; benzene: H_2O_2 mole ratio =1:5.; temperature = 75°C; time =12 h. [b] C_B= Conversion of benzene; [c] S_P = Selectivity to phenol. [d] Y_P=Yield of phenol.

Table 3. Activity of the $CuCr_2O_4$ Spinel nanoparticles catalysts over different substituted benzenes in liquid phase oxidation [a]

Entry	Substrate	Main Product	C_S [b] (%)	S_P[c] (%)	Y_P[d] (%)
1			65.0	75.0	48.8
2			55.0	90.0	49.5
3			57.0	97.0	55.3
4			1.0	>99	1
5			0.2	>99	0.2
6		-	-	-	-
7			75.0	68.0	51.0
8			82.0	57.0	46.8
9			78	65.5	51.1
10			55	70	38.5

[a] Reaction Condition: solvent (MeCN) = 10 ml; substrate =1g; catalyst= 0.05g; benzene: H_2O_2 mole ratio =1:5; temperature = 75°C; time =12 h. [b] C_S= Conversion of substrate. [c] S_P = Selectivity to product. [d] Y_P=Yield of product.