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PAPER

Highly active mesoporous chromium silicate catalysts in side-chain oxidation of alkylaromatics†

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We approach a green method in the production of alkylaromatic ketones over hexagonally ordered mesoporous CrSBA-15 catalysts, which were used, in green routes, in the liquid-phase oxidation of alkylaromatics. A promising chemical treatment method was used with ammonium acetate solution to remove the toxic nature of non-framework chromium oxides deposited on the surface of calcined CrSBA-15(8), and the obtained green mesoporous CrSBA-15(8) catalyst was used to find its catalytic activity while the recyclability of mesoporous CrSBA-15 catalysts was also studied. Particularly, the mesoporous CrSBA-15 catalysts synthesized with a variety of chromium contents were extensively used in the production of acetophenone (AP═O) with various reaction parameters. On the basis of all catalytic results, the mesoporous CrSBA-15(8) catalyst produced a higher selectivity of alkylaromatic ketones (76–100%) as compared to other CrSBA-15 catalysts and was found to be a highly active, recyclable and promising heterogeneous catalyst for selective synthesis of alkylaromatic ketones.

1. Introduction

Selective side chain oxidation of alkylarenes to aromatic ketones is one of the most important fundamental reactions,[1] is mainly based on the conventional homogeneous catalysis in chemical industries and is mostly carried out with acetic acid as the solvent as well as molecular oxygen as the consumable oxidant.[2] In these catalytic oxidations the poisonous Cr(VI) reagents are also used as the homogeneous catalysts.[3] However, the conditions of the conventional method are often harsh, the reagent mixture is corrosive and highly toxic. The reaction temperature is high and demands the use of autoclave reactors, which are made of expensive raw materials due to the corrosive medium. Therefore, there is a need for the development of new heterogeneous catalysts in the production of alkylaromatic ketones with higher selectivities.

Ethylbenzene (EB) oxidation is one of the alkylaromatic oxidations and is largely used in the production of acetophenone (AP═O). AP═O is one of the key products in the manufacture of pharmaceuticals, resins, alcohols and tear gas (chloroacetophenone) and is also used as a component in perfumery as well as a solvent for cellulose ethers. AP═O is produced by the liquid-phase EB oxidation using molecular oxygen or air as the oxidizing agent over homogeneous chromium containing inorganic/organic catalysts[2] and organometallic catalysts.[4,5] Although homogeneous catalysts exhibit excellent activity and selectivity, the technical problems encountered in their applications, such as the difficulty in product separation and self aggregation of active sites, have slowed down their industrial applications. These catalytic systems also create other problems such as handling, catalyst recovery, recycling, environmentally unsuitable and highly produced tarry wastes. To overcome these problems, solid acid catalysts have been successfully used in the liquid phase oxidation of alkylarenes.[6–17] The heterogeneous chromium reagents are widely used as catalysts for the oxidation of alkylaromatic compounds in organic chemistry.[18] Therefore, several chromium containing solid materials have been utilized as the catalysts in liquid-phase oxidation of alkylaromatics with a variety of oxidizing agents.[6–19] For example, the microstructured CrAPO-5 catalyst produced less EB conversion with higher AP═O selectivity under liquid phase EB oxidation because its small pore diameter (~0.73 Å) restricts the diffusion of reactants/intermediate and products.[6,7] In recent years, the mesoporous CrMCM-41 catalyst was used in the EB oxidation to improve the EB conversion with higher AP═O selectivity because it has larger uniform pore size than CrAPO-5.[6,7,20] In 2007, Selvaraj and co-workers reported the well hexagonally uniform pore structured CrSBA-15.[13–17] The mesoporous CrSBA-15 catalysts have been successfully used for the synthesis of very useful fine chemicals with higher selectivities, and have superior catalytic activities than CrMCM-41 due to the higher Cr species coordinated on the thick silica pore walls.[13–17] However, to the best of our knowledge, the CrSBA-15 catalysts have not been used in oxidation of EB, and the production of

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alkylaromatic ketones over CrSBA-15 has not been extensively reported, in the open literature so far.

In our report, for selective synthesis of alkylaromatic ketones, the mesoporous CrSBA-15 catalysts have been efficiently used in the liquid-phase oxidation of alkylaromatics. Particularly, the selective synthesis of acetophenone (AP═O) over mesoporous CrSBA-15 catalysts has been extensively studied with various reaction parameters. The catalytic results obtained from all mesoporous catalysts are correlated and compared for the selective synthesis of alkylaromatic ketones.

2. Experimental

2.1. Materials

For the preparation of mesoporous Cr-containing silica catalysts, all chemicals *viz.* triblock copolymer poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), tetraethylorthosilicate (TEOS, 98%), hydrochloric acid (HCl, 37%), and Cr(III) nitrate nonahydrate (CN, 99%) were purchased from Aldrich Chemical Inc. and used as received without further purification.

For the selective synthesis of alkylaromatic ketones, all chemicals *viz.* ethylbenzene (EB, 99.8%), electron donating (ED) group substituted EBs, such as 1-ethyl-4-methoxybenzene (4-ethylanisole, 97%) and 1-ethyl-2-methoxybenzene (2-ethylanisole, 99%), and electron withdrawing (EW) group substituted EBs, such as 1-chloro-4-ethylbenzene (97%), 1-ethyl-4-nitrobenzene, 4-ethylphenol (99%), 1-chloro-2-ethylbenzene, 1-ethyl-2-nitrobenzene (96%) and 2-ethylphenol (99%), *t*-butylhydrogen-peroxide (TBHP, 70%), hydrogen peroxide (30% H_2O_2), acetonitrile (MeCN, 99.8%), chlorobenzene (CB, 99.8%) and methanol (MeOH, 99.8%), were also purchased from Sigma-Aldrich (USA) and TCI (Japan) Chemical Inc. and used as received without further purification.

2.2. Synthesis and characterization of CrSBA-15 and CrMCM-41

As-synthesized mesostructured CrSBA-15 catalysts with n_{Si}/n_{Cr} = 8, 16, 20, and 50 were synthesized with a molar gel composition 1 TEOS/0.02–0.125 Cr_2O_3/0.016 P123/0.43 HCl/127 H_2O using the pH-adjusting direct hydrothermal method according to a previously published procedure.[13,17] Finally, the samples were calcined at 813 K in air for 6 h for complete removal of the template. The calcined mesoporous samples with their corresponding n_{Si}/n_{Cr} ratios of 8, 16, 20, and 50 are denoted as CrSBA-15(8), CrSBA-15(16), CrSBA-15(20), and CrSBA-15(50). The mesoporous CrMCM-41(40) catalyst with n_{Si}/n_{Cr} = 40 was synthesized using cetyltrimethylammonium bromide as the structuring agent with a gel molar ratio 1 SiO_2/0.025 Cr_2O_3/0.25 CTMABr/100 H_2O under hydrothermal method according to a previously published procedure.[12]

2.3. Characterization

The calcined, washed and recyclable CrSBA-15 mesoporous catalysts were characterized by ICP-AES, XRD, N_2 sorption isotherms, ESR, ^{29}Si MAS NMR, UV-vis DRS, FE-SEM and TEM according to the published procedure.[13,17] The mesoporous CrMCM-41(40) catalyst was also characterized by ICP-AES, XRD, N_2 sorption isotherms and UV-vis DRS according to a published procedure.[12]

2.4. Oxidation of alkylaromatics

All the chemicals, for side-chain oxidation of alkylaromatics, were purchased from Aldrich Chemical Inc., and used as received without further purification. In order to explain the liquid-phase oxidation of alkylaromatics, oxidation of EB to AP═O was taken as an example and performed under vigorous stirring in a thermostatted quartz vessel reactor with various reaction parameters. In a typical experimental procedure, 0.1 g of CrSBA-15(8) was taken in the reactor with 20 mmol of EB and 20 ml of CB solvent. After that, the reactor was stirred constantly with slowly raising the temperature to 393 K. Then, the reactant mixture was continuously refluxed for 10 h after adding 40 mmol of *t*-butylhydroperoxide (TBHP) through the septum. After completion of the reaction, the products were collected by recovering CrSBA-15(8). To find the best catalyst, the diverse Cr-containing mesoporous catalysts were used for the oxidation of EB under similar reaction conditions. Various reaction parameters such as time, temperature, stoichiometric molar ratios of reactant (EB-to-TBHP) were studied to find the best reaction conditions over CrSBA-15(8). For the identification of a better solvent over CrSBA-15(8), the oxidation of EB was carried out with different solvents like MeCN, CB and MeOH. The oxidation of EB was also carried out with hydrogen peroxide (H_2O_2, 30%) with MeOH. Furthermore, using the mesoporous CrSBA-15 catalysts the side-chain oxidation of other alkylaromatics, such as 4-ethylanisole, 1-chloro-4-ethylbenzene, 1-ethyl-4-nitrobenzene, 4-ethylphenol, 2-ethylanisole, 1-chloro-2-ethylbenzene, 1-ethyl-2-nitrobenzene, 2-ethylphenol, was extensively performed using a vigorously stirred thermostatted glass vessel reactor under various reaction conditions.

The collected organic products after completion of the reaction were extracted using ether from the resulting mixture cooled at room temperature and analyzed with authentic samples by gas chromatography (GC) employing a ZB-5 capillary column. Additionally, the products were further confirmed using combined gas chromatography-mass spectrometry (GC-MS, Hewlett G1800A).

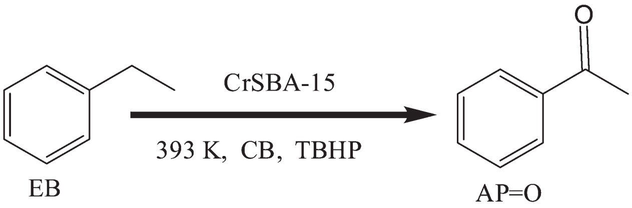
2.5. Experimental procedures for stability of catalyst

The used Cr-containing mesoporous silica catalysts, such as CrSBA-15(8) and CrSBA-15(50), were regenerated by washing and calcination, as reported in our published method,[15] and reused (0.1 g of catalyst) in the side-chain oxidation of alkylaromatics to determine their catalytic stabilities. The washed CrSBA-15(8) catalyst was also prepared using our published method[15] and used (0.1 g of catalyst) in this reaction to find its catalytic activity. After completion of each catalytic reaction, the catalyst was filtered and analyzed by ICP-AES to determine the percentage of Cr, and the conversion of alkylaromatics and selectivity of ketones were calculated with the standard formulas followed by analysis of the results of GC and GC-MS.

3. Results and discussion

The liquid-phase oxidation of alkylaromatics over the CrSBA-15 catalyst (Scheme 1), which proceeds *via* a radical-chain mechanism.[15,21] Initially, for the side-chain oxidation of alkylaromatics, selective synthesis of AP═O was investigated using the reaction conditions noted in Table 1. This reaction also produces minor byproducts such as 1-phenylethanol (PE–OH) and ethylbenzene hydroperoxide (EHP). In order to increase the AP═O selectivity, the catalytic activity increases in the following order, CrSBA-15(8) > CrSBA-15(16) > CrSBA-15(20) > CrMCM-41(40) > CrSBA-15(50). CrSBA-15(8) exhibits the best performance with 95.6% EB conversion as well as 98.2% AP═O selectivity, and its catalytic activity is higher than other CrSBA-15 catalysts due to the higher loading of tetrahedral Cr^{5+}/Cr^{6+} species on the inner pore walls of SBA-15, resulting in a huge number of accessible active sites because the tetrahedral Cr^{5+}/Cr^{6+} species create a large number of Lewis acid sites on the inner surface of the pore walls. The characteristic results of ICP-AES, XRD, N_2 sorption isotherms, ESR, UV-vis DRS strongly support that the CrSBA-15(8) catalyst has higher catalytic activity than other Cr-containing mesoporous catalysts; ICP-AES studies show that the amounts of Cr-ions incorporated on the silica pore walls of CrSBA-15(8) are higher than those of other CrSBA-15 catalysts.[13] Furthermore, the results of ^{29}SiMAS NMR, as shown in Fig. 1S,† prove that the signal intensity of CrSBA-15(8) is much reduced as compared to that of siliceous SBA-15;[13,15,17] this observation clearly supports the stabilization of chromium ions *via* silanol groups (defect sites). As shown in Fig. 2S and 3S,† the results of ESR and UV-vis DRS prove that the amounts of tetrahedral Cr^{5+}/Cr^{6+}-ions coordinated to Si^{4+} on the silica walls of the calcined CrSBA-15(8) catalyst are higher than those of other CrSBA-15 catalysts.[13,15,17] Even though the huge amounts of Cr-ions are incorporated into the silica pore walls, the results of N_2 sorption isotherms and XRD reveal that the textural (pore size, pore volume and wall thickness) and structural (unit cell size) parameters of the CrSBA-15(8) catalyst are higher as compared to other CrSBA-15 catalysts.[13,15,17] The results of elemental composition, structural and textural properties of CrSBA-15 catalysts are listed in Table 1S.† Additionally, comparing the results of similar chromium content of mesoporous catalysts (Table 1S†), CrSBA-15(20) has significantly higher catalytic activity as compared to CrMCM-41(40), as shown in Table 1. This reaction is also carried out using SiSBA-15 synthesized by the pH-aDH method.[13] In this case, ~15% EB conversion as well as ~82% EHP is obtained (Table 1), thus indicating that the major activity is only due to chromium species incorporated on the silica pore walls of SBA-15. On the basis of catalytic activities, it is noted that the well-ordered mesoporous catalyst plays an important catalytic role in the production of AP═O with higher selectivity.

Among the other Cr-containing 2D mesoporous catalysts, CrSBA-15(8) and CrSBA-15(50) produce the highest and lowest AP═O selectivity, accordingly. From this information, we have used the catalysts *viz*. CrSBA-15(8) and CrSBA-15(50) as reusable catalysts, under the same reaction conditions noted in Table 1, to find their catalytic stabilities. Initially, the used CrSBA-15 catalysts usually produce less product selectivity because most of the active sites can be screened by unreacted organics that make one of the sintering effects on the surface of catalysts, and hence the catalysts, before reuse in this catalytic reaction, need to be regenerated by washing and calcination. The catalysts, such as CrSBA-15(8) and CrSBA-15(50), were washed four times with acetone and dried at 393 K overnight. Finally the catalysts were calcined at 773 K for 6 h in air for the removal of the organics and unreacted DPM molecules, completely. The treated catalysts, such as CrSBA-15(8) and CrSBA-15(50), were reused for this reaction (Table 1). The EB conversion as well as AP═O selectivity decreases in the first two runs (not shown in Table 1). On the basis of the first two runs, the leaching of non-framework chromium species, such as toxic chromium



Scheme 1 Oxidation of EB over CrSBA-15.

Table 1 Oxidation of ethylbenzene over Cr-containing mesoporous silica catalysts[a]

	n_{Si}/n_{Cr} ratio			Product selectivity (%)		
Catalysts	Gel	Product[b]	EB conversion (%)	AP═O	PE–OH	EHP
CrSBA-15(8)	8	9.9	95.6	98.2	1.8	—
CrSBA-15(16)	16	17.3	82.3	84.5	10.3	5.2
CrSBA-15(20)	20	45.0	75.6	78.7	15.6	5.7
CrSBA-15(50)	50	99.8	54.3	56.7	12.5	30.8
CrMCM-41(40)	40	45.0	69.5	71.3	12.5	16.2
CrSBA-15(8)[c]	—	12.4	90.4	95.5	4.5	—
CrSBA-15(50)[c]	—	99.9	45.1	54.5	5.2	40.3
CrSBA-15(8)[d]	—	12.3	90.5	95.9	4.1	—
SiSBA-15	—	—	15.2	17.3	1.0	81.7

[a] *Reaction conditions*: 0.1 g of catalyst, 1 : 2 mmol ratio of EB to TBHP (20 mmol of EB : 40 mmol of TBHP), reaction time = 10 h, 20 ml of CB, T = 393 K. [b] n_{Si}/n_{Cr} ratios of products are determined by ICP-AES. [c] The results obtained by regenerated catalysts used in the 4th run. [d] Washed catalyst.

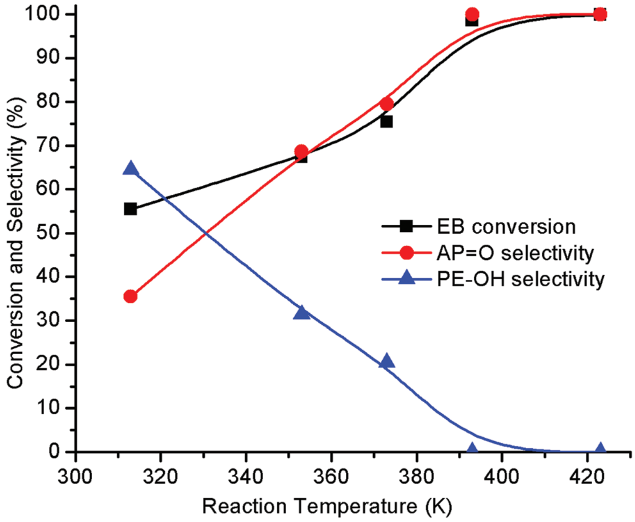


Fig. 1 Oxidation of EB with various reaction temperatures. Reaction conditions: 0.1 g of CrSBA-15(8) catalyst, 1 : 2 mmol ratio of EB to TBHP (20 mmol of EB : 40 mmol of TBHP), reaction time = 10 h, 20 ml of CB.

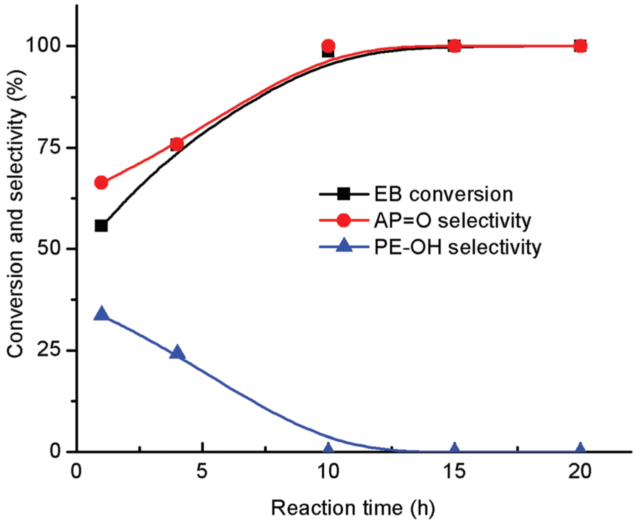


Fig. 2 Oxidation of EB with different reaction times. Reaction conditions: 0.1 g of CrSBA-15(8) catalyst, 1 : 2 mmol ratio of EB to TBHP (20 mmol of EB : 40 mmol of TBHP), reaction temperature = 393 K, 20 ml of CB.

oxide, polychromate and pentavalent chromium oxide, is observed on the catalytic surface while the catalytic activity is slightly decreased, as shown in Table 1. But, the EB conversion as well as AP═O selectivity remains constant in the 4th run, indicating that the active tetrahedral chromium species could not be further leached on the mesoporous matrix, which is in good agreement with the ICP-AES results of filtrate solutions where no active chromium species was detected in the solution. We suspect that in this reaction the aqueous *t*-butanol generated as a byproduct is responsible for the extraction of non-framework pentavalent chromium species in CrSBA-15 catalysts. Moreover, the washed CrSBA-15(8) is also used as a green mesoporous catalyst in this reaction to find its catalytic stability and its effect is nearly similar to the catalytic results obtained in the 4th run of CrSBA-15(8), as shown in Table 1. From this evidence, it is interesting to note that the catalysts used in the 4th run show nearly the same conversion, indicating that the leaching of active chromium is not observed on the surface of the SBA-15 matrix. Additionally, ICP-AES analysis confirms the absence of Cr species after analyzing the reaction mixture. After finding the results of the four runs, the hot-catalyst filtration experiments were also carried out twice at 393 K during oxidation of EB over CrSBA-15(8). In this case, the filtrate solution gives a very low EB conversion (10.5%) with trace amounts of AP═O selectivity (<5.3%) due to leaching of non-framework toxic-chromium oxides on the surface of the catalyst, indicating that the oxidation of EB takes place on the surface of CrSBA-15(8) and is found to be a true heterogeneous process.[22] As an important point, the UV-vis DRS results, as shown in Fig. 3S,† clearly confirm that the non-framework toxic-chromium oxides, such as polychromate and Cr(VI) oxide species, are completely removed by washing treatments, and similar results are almost observed from the hot-catalyst filtrate solution of CrSBA-15(8). Furthermore, the characteristic results of ICP-AES, XRD, N_2 sorption isotherms and UV-vis DRS strongly prove that the used catalysts, such as washed CrSBA-15(8) and recyclable CrSBA-15(8), show that their structural and textural parameters (Table 1S and Fig. 4S†), including the environments of Cr species coordinated on the surface of SBA-15, are still maintained.[15,17] It is observed on the basis of recycling results that CrSBA-15(8) is exclusively found to be the unprecedented catalyst among the other Cr-containing mesoporous catalysts.

Since CrSBA-15(8) is the best active catalyst among the other CrSBA-15 catalysts, it is further used in this reaction with different reaction parameters such as temperature, time and ratios of reactants. The oxidation of EB is conducted at different reaction temperatures as well as times using the reaction conditions noted in Fig. 1 and 2. When the reaction temperature and time are decreased from 393 K to 313 K and 10 to 1 h, respectively, the rate of both ethylbenzene consumption and AP═O formation decreases. The feasible EB conversion decreases with decreasing temperature or time. This may be due to the lower activity of Lewis active sites on the surface of the catalyst at a lower temperature or time, which cannot be promptly supported for the decomposition of EHP into PE–OH whereas the PE–OH converted into AP═O is low. Moreover, the EB conversion as well as AP═O selectivity is not significantly increased when the reaction temperature and time are increased to 403 K and 12 h, respectively, under similar reaction conditions. However, at above 403 K, the EB conversion as well as AP═O selectivity slightly decreases because the self decomposition of TBHP proceeds faster and it does not participate effectively in the process of side-chain oxidation of EB. In contrast the PE–OH selectivity increases from 390 to 310 K but decreases after 390 K because of increasing AP═O selectivity. When this catalytic reaction is carried out with a 1 : 2 ratio of EB to TBHP using the reaction conditions noted in Fig. 3, higher EB conversion as well as AP═O selectivity is obtained. A reason may be that the mixture of reactants in the ratio of 1 : 2 reaches an equilibrium state and the reactants react mutually with each other on the catalytic surface without deactivation. The conversion as well as selectivity decreases in other EB to TBHP ratios of 1 : 1, 1 : 3 and 2 : 3. Note that overoxidation products, such as benzoic acid and

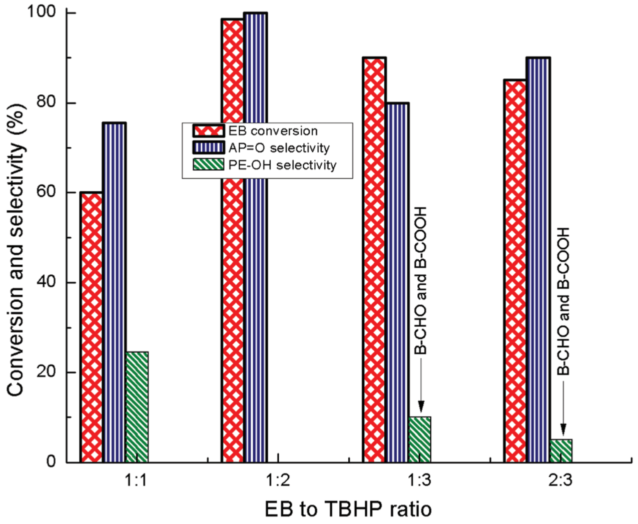


Fig. 3 Variation of EB to TBHP ratios over CrSBA-15(8). Reaction conditions: 0.1 g of CrSBA-15(8) catalyst, reaction temperature = 393 K, reaction time = 10 h, 20 ml of CB.

Table 2 Oxidation of ethylbenzene with different solvents over CrSBA-15(8)[a]

Temp. (K)	Solvent (20 ml)	EB conversion (%)	Product selectivity (%)		
			AP═O	PE–OH	EHP
393	CB	98.6	100	—	—
353	MeOH	88.3	100	—	—
353	MeOH[b]	98.7	100	—	—
353	MeOH[c]	90.5	100	—	—
343	MeCN	58.4	80.4	10.9	8.7
343	MeCN[b]	17.6	56.0	5.3	38.7
393[d]	—	53.0	67.0	2.0	31.0

[a] *Reaction conditions*: 0.1 g of CrSBA-15(8) catalyst, 1 : 2 mmol ratio of EB to TBHP (20 mmol of EB : 40 mmol of TBHP), reaction time = 10 h. [b] 20 mmol of 30% H_2O_2 was used instead of TBHP. [c] Washed CrSBA-15(8) catalyst. [d] Reaction time = 24 h.

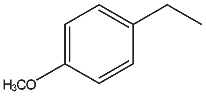
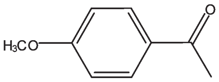
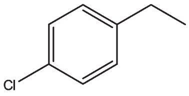
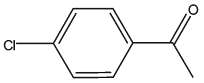
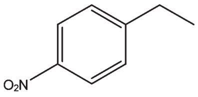
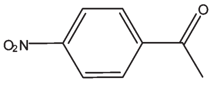
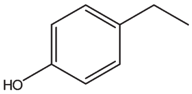
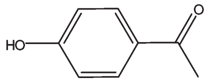
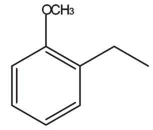
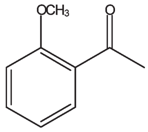
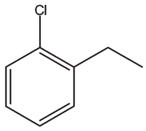
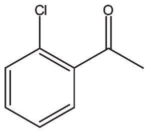
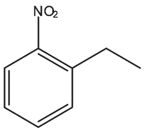
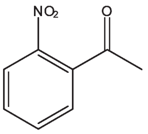
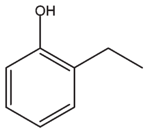
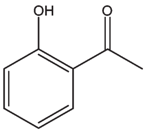
benzaldehyde, form when TBHP is increased (1 : 3), and the diffusion rate of CrSBA-15(8) and the rate of EB conversion decrease in the ratios of 1 : 1 and 1 : 3 which could not be used to improve the higher AP═O selectivity because of the unreacted organics deposited on the inner pore walls. Comparing the results of all catalytic parameters, it is noteworthy that the EB oxidation at 393 K for 10 h with a 1 : 2 ratio of EB to TBHP over CrSBA-15(8) gives higher EB conversion as well as AP═O selectivity.

The oxidation of EB was carried out with different solvents like MeCN, CB and MeOH over CrSBA-15(8) using the reaction conditions noted in Table 2, for obtaining a higher selectivity of AP═O. CB is a common and high-boiling solvent that has the ability to form complexes on the catalytic surface for a long time, and it preferentially attacks the active sites to complete the maximum conversion of EB. When this reaction is carried out with 10 ml of CB under similar reaction conditions, the EB conversion (75%) as well as AP═O selectivity (86%) is much reduced because the high quantity of EB may not be completely dissolved and cannot be completely reacted with TBHP. At 353 K, MeOH gives 88.3% EB conversion with 100% AP═O selectivity. But the EB conversion is still higher as compared to that obtained in TBHP when the reaction is carried out with H_2O_2 instead of TBHP in the presence of MeOH under similar reaction conditions. Additionally, the EB conversion over washed CrSBA-15(8) is almost similar in both solvents, such as CB and MeOH, as shown in Tables 1 and 2. Even though MeCN is a green solvent, it creates low catalytic activity on the surface of the catalyst and produces low EB conversion. When the liquid-phase oxidation of EB is carried out with H_2O_2 instead of TBHP in the presence of MeCN at 343 K under similar reaction conditions, the EB conversion as well as AP═O selectivity is very low because the EHP could not be completely oxidized whereas the EHP converted into PE–OH is much less. For the confirmation of the catalytic activity decrease by the solvents, this reaction was carried out without any solvent at 393 K with a higher reaction time (24 h). In this case, the EB conversion (53%) and AP═O selectivity (67%) are obtained. From the above experiments, the unsuitable solvents could not be promoted to higher catalytic activity and may have blocked most of the active sites on the surface of catalyst.[23] Comparing the catalytic activity obtained with different solvents, it is found that CB with TBHP at higher temperature (393 K), and MeOH with H_2O_2 at lower temperature (353 K), are the best solvents for the highly selective synthesis of AP═O.

To explore the scope and limitations of this catalytic system over the CrSBA-15(8) catalyst, the side-chain oxidation of *p*-substituted EBs, such as 4-ethylanisole, 1-chloro-4-ethylbenzene, 1-ethyl-4-nitrobenzene and 4-ethylphenol, and *o*-substituted EBs, such as 2-ethylanisole, 1-chloro-2-ethylbenzene, 1-ethyl-2-nitrobenzene and 2-ethylphenol, has been studied using the reaction conditions noted in Table 3. As shown in Table 3, the mesoporous CrSBA-15(8) catalyst exhibits outstanding performance in oxidation of the ED group substituted at the *p*-position of EB and produces higher ketone selectivity (entry 1). But in the case of the ED group substituted at the *o*-position of EB, the ketone selectivity is much reduced because of steric effects (entry 5), a similar trend has already been reported in the literature.[24] Among all the EW groups (*e.g.*, OH and NO_2) substituted at the *p*-position of EBs, the oxidation of *p*-Cl-substituted EB over CrSBA-15(8) is excellent and produces 97% ketone selectivity (entries 2–4), as shown in Table 3. However, in the case of EW groups (*e.g.*, Cl, OH and NO_2) substituted at the *o*-position of EBs the ketone selectivity decreases because of steric effects (entries 6–8). Finally, the oxidation of *p*-substituted EBs (ED and EW groups) has positive effects on the ketone selectivity whereas the oxidation of *o*-substituted EBs (ED and EW groups) has somewhat negative effects on the ketone selectivity.

The recyclable CrSBA-15(8) catalyst has also been reused in the side-chain oxidation of *p*- and *o*-substituted EBs under similar reaction conditions, and the conversion of *p*- and *o*-substituted EBs as well as the selectivity of ketones is obtained as shown in Table 3. Based on the catalytic activity in the oxidation of each *p*- and *o*-substituted EB, it is noteworthy that the catalytic activity of this catalyst remains constant in the 4th run, and

Table 3 Selective oxidation of ethylbenzene compounds over CrSBA-15(8)[a]

Entry no.	Substrate	Ketone product	Conversion (%)	Selectivity of ketone (%)	Selectivity of alcohol (%)
1	 1-ethyl-4-methoxybenzene	 1-(4-methoxyphenyl)ethanone	98 95^b 96^c	100 98^b 98^c	— 2^b 2^c
2	 1-chloro-4-ethylbenzene	 1-(4-chlorophenyl)ethanone	90 86^b 87^c	97 94^b 94^c	3 6^b 6^c
3	 1-ethyl-4-nitrobenzene	 1-(4-nitrophenyl)ethanone	73 67^b 68^c	91 85^b 85^c	9 15^b 15^c
4	 4-ethylphenol	 1-(4-hydroxyphenyl)ethanone	80 76^b 75^c	94 89^b 88^c	6 11^b 12^c
5	 1-ethyl-2-methoxybenzene	 1-(2-methoxyphenyl)ethanone	87 84^b 85^c	93 89^b 88^c	7 11^b 12^c
6	 1-chloro-2-ethylbenzene	 1-(2-chlorophenyl)ethanone	67 63^b 63^c	88 83^b 83^c	12 17^b 17^c
7	 1-ethyl-2-nitrobenzene	 1-(2-nitrophenyl)ethanone	61 59^b 58^c	84 79^b 78^c	16 21^b 22^c
8	 2-ethylphenol	 1-(2-hydroxyphenyl)ethanone	68 65^b 64^c	81 76^b 77^c	19 24^b 23^c

[a] *Reaction conditions*: 0.1 g of CrSBA-15(8) catalyst, 20 ml of CB, reaction time = 10 h, temperature = 373 K, 1 : 3 ratio of substrate-to-TBHP (20 mmol of substrate, 60 mmol of TBHP). [b] The results obtained by regenerated CrSBA-15(8) catalyst used in the 4th run. [c] Washed CrSBA-15(8) catalyst.

the percentage of Cr-content remains constant. Furthermore, washed CrSBA-15(8) was also used in these reactions to find its catalytic activity. This catalytic activity is nearly similar to that of used CrSBA-15(8) in the 4th run, as shown in Table 3. Overall, on the basis of the catalytic results, it is noted that CrSBA-15(8) is a highly active, recyclable and unprecedented heterogeneous catalyst for the highly selective synthesis of ketones in the oxidation of *p*- and *o*-substituted EBs. Comparing the results with the literature, the CrSBA-15(8) catalyst has exceptional catalytic activity in the oxidation of *p*- and *o*-substituted EBs among the other solid catalysts.[18,20,25,26]

4. Conclusions

The mesoporous CrSBA-15 catalysts have been successfully used in the oxidation of alkylaromatics and produced the higher selectivity of alkylaromatic ketones. From the washing studies, the green CrSBA-15(8) catalyst has been completely recovered from the toxic nature of non-framework chromium oxide and has been successfully used in these oxidations to find its catalytic activity. In addition to finding the catalytic stabilities of CrSBA-15 catalysts, the recyclable and hot-catalytic experiments have been successfully studied. Based on the recyclable studies in the oxidation reactions, it reveals that a huge number of tetrahedral chromium species have successfully participated in the Lewis active sites on the silica surface of the CrSBA-15(8) catalyst. From the results of hot-catalyst filtration, it is found that CrSBA-15(8) is a true heterogeneous catalyst in the oxidation reactions. Based on all the catalytic results, CrSBA-15(8) is found to be a highly active, recyclable and environmentally friendly solid catalyst.

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